Enhancement of Solubilization (PAHs/Water) & Rheological Behavior at the Interfaces (Air, Oil/Water) in Presence of Surfactants & Additives

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By

SUBHASHREE BEHERA

(214CH1095)

Under the supervision of

Prof. Santanu Paria

DEPARTMENT OF CHEMICAL ENGINEERING

NATIONAL INSTITUTE OF TECHNOLOGY

ROURKELA-769008

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DEPARTMENT OF CHEMICAL ENGINEERING
NATIONAL INSTITUTE OF TECHNOLOGY
ROURKELA-769008, INDIA

CERTIFICATE

This is to certify that the project report entitled, "**Enhancement of Solubilization (PAHs/Water) & Rheological Behavior at the Interfaces (Air, Oil/Water) in Presence of Surfactants & Additives**." submitted as thesis by Subhashree Behera (214CH1095) for the requirements of award of Master of Technology in Chemical Engineering Department of National Institute of Technology, Rourkela under my supervision.

Date:

Place: Rourkela

Prof. Santanu Paria
Department of Chemical Engineering
NIT Rourkela

DECLARATION

I declare that this written submission represents my ideas in my own words and where others' ideas or words have been included, I have adequately cited and referenced the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that any violation of the above will be cause for disciplinary action by the Institute and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.

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214CH1095

Date:

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Date:

Place: Rourkela

SUBHASHREE BEHERA

214CH1095

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NOMENCLATURE

CMC	Critical Micellar Concentration
MSR	Molar solubilization ratio
K_m	Partition coefficient
NaCl	Sodium Chloride
$CaCl_2$	Calcium Chloride
Na_2SO_4	Sodium Sulphate
CTAB	Cetyl trimethylammonium bromide
IFT	Interfacial tension
ST	Surface tension
DDAB	Didodecyldimethyl ammonium bromide
X_1	Mole fraction
C	Concentration
G’	Storage Modulus
G”	Loss Modulus
SDBS	Sodium dodecylbenzene sulfonate

ABSTRACT

Solubilization of two immiscible phases can be achieved with the help of additives such as surfactants as it has wide range of applications in many industries. In order to have better solubilization the rheological behaviour of additive added interface plays a critical role. In this thesis solubilization of naphthalene, a double ringed PAH and anthracene, a triple ringed PAH, in the micellar solution of cationic surfactant CTAB has been studied in order to remove PAHs from contaminated soil and ground water. Effect of three electrolytes NaCl, Na_2So_4 and $CaCl_2$ on the solubilization of naphthalene and anthracene as additives in the presence of cationic surfactant CTAB is also examined. Different physicochemical properties such as critical micelle concentration (CMC), molar solubilization ratio (MSR) and partition coefficient (K_m) have been estimated for the cationic surfactant and cationic surfactant with different electrolyte solutions. The cationic surfactant system showed a synergetic behaviour and a maximum synergism was observed for the cationic surfactant in the presence of higher valence counter ion electrolyte. The synergism of CTAB with electrolyte is also confirmed by 1D ^1H NMR study. The rheology at air/water and oil/water interface has been presented using cationic single chain surfactant CTAB, double chain cationic surfactant DDAB, non-ionic surfactant IGEPAL CO-630, anionic surfactant SDBS and TiO_2 nanoparticle of size 21 nm. In addition to these rheology studies for surfactant mixture of DDAB & IGEPAL CO 630, CTAB in presence of NaCl and mixture of SDBS with TiO_2 has been studied extensively at air/water and oil/water interfaces. Additives like electrolyte and nanoparticle are used in order to reduce the consumption of costly surfactant as well as to reduce their environmental impact. Synergism was observed for all the mixed system but SDBS with TiO_2 nanoparticle showed more stable oil/water interface by reducing the viscosity and linear viscoelastic parameters at the interface.

KEYWORDS: Solubilization, PAHs, interface, surfactant, electrolyte, nanoparticle, mixture.

ORGANIZATION OF THESIS

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INTRODUCTION

This chapter includes a brief introduction to solubilization of polycyclic aromatic hydrocarbons in aqueous media and rheological behavior at air, oil/water interface with the help of different additives along with the motivation to study this has been presented. Emphasis has been given on the performance of co-additives to enhance the surfactant capability, which is also the focus area of the research. The details of the research work carried out,has been presented in this chapter.

1.1 Background and motivation

Solubilization has become an inevitable part of human day-to-day life, starting from toothpaste, handwash, shampoo, conditioner, confectionery, cream, medicines, enhanced oil recovery to manage the ecosystem all involve the fundamental mechanism of solubilization. The practical importance of solubilization involves the fact that it can dissolve substances in solvents in which they are normally not soluble [1].Solubilization of hydrophobic substances (oil, polycyclic aromatic hydrocarbons) in aqueous media has received wide attention because of its diversified applications in food, pharmaceuticals, cosmetics, paint, dye, enhanced oil recovery and also for environmental management. These applications involve solubilization of oil in water to get emulsion or to remove toxic polycyclic aromatic hydrocarbons (PAHs)/hydrophobic organic contaminants (HOCs), heavy metals etc. from contaminated soil and ground water. From these, this study is based on the PAHs solubilization in water medium. PAHs possess teratogenic, carcinogenic and mutagenic properties which have an adverse effect on ecosystem and it cannot be removed from contaminated sites because of its high electrochemical stability, high water insolubility [2]. By surfactant enhanced remediation (SER) process PAHs can be solubilized in aqueous medium by using surfactants which enhances the cleaning of soils and ground water contaminated with HOCs/PAHs by transferring the pollutants to the micellar core of surfactant. Currently SER is the widely used remediation process because of its high efficiency and environment friendly nature [3-9]. Practically, the mixing of hydrophobic substances in water is not possible as their interfaces is at different energy levels and are unstable. To have a stable interface surfactant plays crucial role. The micellar surfactant core carries any hydrophobic

substance making them soluble in water. The performance of surfactant can be enhanced by different additives such as electrolytes, nanoparticles, polymers, proteins etc. depending on different applications.

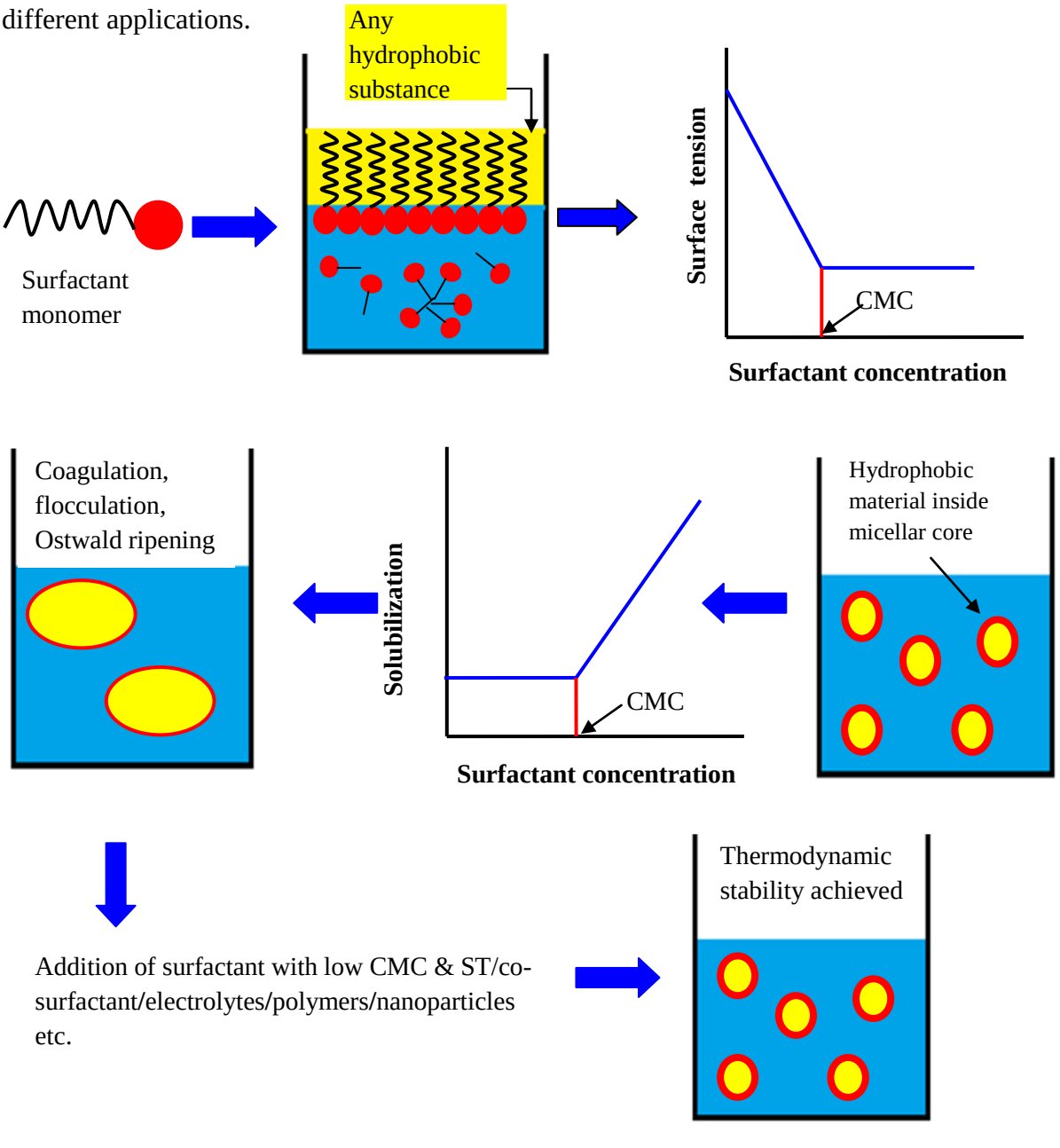


Fig. 1.1: Surface/interfacial tension reduction and solubilization mechanism

In order to have better solubilization the additive added interface plays a critical and important role. To understand the interface which is the limiting step for solubilization, rheology study was carried out. Rheological study helps to define the stability of complex structures such as emulsions, suspensions, sewage, mud etc. falls under the class of soft matters. Oscillatory and shear rheology studies are the fundamental tools to understand such behavior. Oscillatory rheology involves the study of storage (G') and loss (G") modulus

which characterizes the elastic and viscous behavior of matters respectively. The timedependent rheology of surfactants at air, oil/water interface is imperative for emulsion preparation in paints, cosmetics, pharmaceuticals, enhanced oil recovery, food industry, polishes, pesticides, textile industry, water and sewage treatment emulsion preparation, concrete etc[1, 10-15].Therefore rheology at these interfaces is of great concern which predicts its flow behavior, molecular interaction and structure [16]. Besides these it also includes the modification of air, oil/water interfacial rheology for different applications with the help of different additives such as surfactant, nanoparticles, polymers, proteins etc. [17-20].Fundamental mechanism of surfactant adsorption at the interface is a crucial pitch in the knowledge of their functionality and applications [21, 22]. At present, the depiction of adsorbed interfacial layers of surfactant with different additives is essentially done by many fundamental and applied dynamic practices.

Enhancement of solubilization of two immiscible phases and rheology at their interfaces can be modified depending on the application with the help of surfactant and other additives. Surfactants are the most versatile amphiphilic monomers with both hydrophilic head group and hydrophobic tail part.The entire mechanism of surface tension/interfacial tension reduction and solubilization is presented in Fig. 1.1. Surfactants adhere at the surface/interface when added to water resulting reduction in surface tension/interfacial tension i.e. reducing the surface energy required to increase the surface area per molecule. Further addition of surfactant causes formation of micelles above which no further reduction of surface tension occur and that concentration is known as critical micellar concentration (CMC). Additional increase in surfactant concentration above CMC results in more number of denser micelles which carries hydrophobic substances in its micellar core and promotes solubilization. Surfactants help in spontaneous dispersion of immiscible phases. Rogers et al. [23] explained that self-assembling property of surfactant leads to scientific interest and technologically advantageous in modifying the surface properties. Oil/water interface in presence of these surfactant shows viscoelasticity which can be varied to several magnitude with increasing or decreasing its concentration and with the addition of different additives.

In many practical applications mixed surfactants are used over single surfactants as the surface/interfacial properties are quite different from single surfactants and in some cases synergism was significant. One can diminish the environmental crash of toxic surfactant by using it as a mixture with less toxic surfactant whose surface properties are similar. The amounts of surfactant require will also be less for mixture with synergism.

To enhance the property of surfactant electrolytes are being used in many industries. Electrolytes are the most widely used additives to enhance surfactant properties in the industry to achieve optimum solubilization. Electrolytes are used to achieve the surface tension of surfactant solution far before the CMC contributing reduction in surfactant consumption in addition to, it has taken up the liability to enhance the rheological property at the air, oil/water interface. Lowering the tension at the interface by electrolytes contributes to viscosity and modulus reduction giving rise to a stable system [23]. Apart from, Ghosh et al. [15] and Zaman et al. [17] reported in their study that excess concentration of salt can result in coalescence and breaking leading instability. As the CMC can be achieved at a very small concentration of surfactant with the addition of electrolyte, which justifiesthat viscosity reduction can be achieved by lessening surfactant concentration reducing the environmental impact of it. Electrolytes reduces the electrostatic repulsion of the cationic head group, consequently reduces the thickness of electrical double layer facilitating formation of bigger micelles. Rehage et al. proposed that the rheological parameters of cationic surfactant show complex behavior in the bulk solution. However the bulk behavior is pretty much influenced by the interfacial rheological behavior of the system [18].

Nanoparticles are of great concern as it is well known that smaller the particle size more precisely it will adhere at the surface and further surface property modification can be achieved. Nanoparticles have wide spectrum of applications used almost everywhere now-a-days starting from food, pharmaceutical, cosmetics, paints, coating agents, and textile to enhanced oil recovery and many more. They are used to manufacture coalescence free emulsified products as stabilizing particles [25]. Nanoparticles are widely used in cosmetics and pharmaceutical industry as it can penetrate deep inside our skin and body to cure the affected area. Many skin and hair care products are using nanoparticles like TiO_2, ZnO, silica, sulphur etc. to enhance the surface and interfacial properties of oil/water system [26, 27].

An attempt has been made in the following work to enhance the solubilization and rheological parameters by surfactant, surfactant mixtures, electrolytes & TiO_2. The mechanism behind enhanced solubilization due to electrolytes with surfactants has been investigated and the characterization of rheological parameters has been carried out in order to know the extent of stability at the interface in presence of different additives. This work is also indicative of the concentrations at which optimum solubilization and stability achieved at the interfaces.

2 LITERATURE SURVEY

Present chapter deals with the literature review related to solubilization by surfactant & different additives and rheological behavior of these additives at the interfaces (air, oil/water). A particularly detail literature study of the enhancement of solubilization and rheology has also been taken up in the chapter. The chapter also indicates the gap area in which no or very few, research has taken place.

2.1 Solubilization

The solubilization of pyrene (polycyclic aromatic hydrocarbon) in aqueous medium with the help of anionic surfactant (SDS & LDS) in presence of Electrolytes (NH_4Cl, NaCl&LiCl) was studied by Kim et al. [28]. Due to the presence of electrolyte the ion binding affinity increases which causes the increase in aggregation number of surfactant molecules of the micelles resulting in enhanced solubilization capability.Paria et al.[29] used the term molar solubilization ratio (MSR) to explain the solubilization enhancement of Napthalene (PAH) by the application of homologous series of alkylpyridiniumbromide, anionic (SDS), non-ionic nonylphenylethoxylatesurfactants. The experimental investigation showed that with decreasing number of carbon atom in hydrophobic chain MSR value decreases leading to less solubilization and any variation in ethylene oxide in hydrophilic head group of non-ionic surfactant has no effect on MSR value. To reduce the environmental impact and to lessen costly surfactant consumption Ansari et al. [2]synthesized biodegradable Gemini surfactant. Along with that they have used cationic (CPC, CTAC), anionic (SDS, SDBS), non-ionic (Brij–58, TX-100) surfactants to solubilize anthracene and pyrene. Gemini surfactant has lowest CMC and highest MSR value, and anionic surfactant has highest CMC and lowest MSR value. But the mixture of Gemini surfactant with different synthetic surfactants showed synergistic behavior but the maximum synergism was observed with anionic surfactant showing lowest CMC and highest MSR value. Researchers adopted another way to reduce the environmental impact and to reduce surfactant consumption by the application of natural surfactant. Rao et al. [30]used Natural surfactant Sapindusmukorossi (reetha) along with Cationic (CTAB), Anionic (SDBS, SOS, AOT), Non-ionic (TX-100) for surfactant enhanced remediation of naphthalene. Reetha is more effective than anionic surfactant but less effective than non-ionic surfactant. The surfactant mixtureof reetha along with AOT & SOS exhibited

highest synergism as their interaction parameter (β) has more negative value. The more negative is β the more will be surface activity of surfactants. Use of natural surfactant has immense effect to reduce the consumption of costly and toxic surfactants. Similar research has been done by Iglesias et al. [31] they have used saponin as natural occurring surfactant and Non-ionic surfactants (Brij-35, Tween-80, TX-100). The mixture saponon and tween-80 showed lowest CMC resulting highest synergism in phenanthrene solubilization. They also used electrolyte (NaCl), but, as non-ionic and natural surfactants doesn't possess any kind of charge addition of electrolyte has not much elevation in solubilization. Quite different study has been carried out by Lin et al. [32]**.** They have incorporated Polymer (PVP), Organic salt (Bu_4NBr, Pr_4NBr) to augment the solubilization capability of anionic surfactant SDS. Several studies including solubilization experiment has been carried out in order to show the molecular level interaction between polymer-surfactant- organic salt. 1D ^1H NMR studies has been done to show the diffusion of pyrene inside the complex molecular structure of polymer-surfactant- organic salt. The complex structure of PVP and SDS initiates when [SDS]/[Bu4NBr] is greater than 1.1 (or) [SDS]/[Pr4NBr] is greater than 0.6. Accordingly the unset of complex structure formation depends mainly on the concentration of organic salt. Liu et al. [33]and Wei et al. [34]used electrolyte with non-ionic and anionic surfactants and demonstrated through experimental investigation that saline system gives comparatively lower CMC initiating solubilization at a earlier stage and comparatively at low concentration of surfactants. But anionic surfactant results in precipitation and non-ionic doesn't have much interaction with incorporated electrolyte. Yang etal. [35]describes the solubilization by surfactant or mixture of surfactant depends on affinity for hydrophilic chain.

The solubilization of PAHs is mainly influenced by the use of suitable surfactant which gives higher solubilization power and MSR values and lowest CMC with low surface tension values. Cationic, anionic and non ionic as well as natural surfactants have been used in literature to decrease the surface tension and thus increase the solubility. However, if the electrolytes are used along with surfactants the surface tension is further influenced which reduces the consumption of costly surfactant. In place of electrolytes other additives are also used to enhance the solubilisation but addition of electrolyte has been used in wide spectrum. The gap in this area involves electrolytes are mainly used with non-ionic and anionic surfactants and very few studies has been done with cationic surfactant with which it is expected to show more synergism and the effect of increased valence electrolyte on solubilization by surfactant has not yet been carried out.

2.2 Additive added interfacial (air, oil/water) rheology

Many research works involving rheology at air, oil/water interface has been carried out till now. Researchers used different additives such as surfactants, nanoparticles, polymers etc. and their mixture to stabilize the interface and to enhance their rheology at the interface for different applications. Some previous works on rheology at air, oil/water interface is tabulated in table 2.1.

Table 2.1: previous studies on air, oil/water interface stabilized by different stabilizers.

Reference	**Additives used**	**Characterization Parameters**	**Applications**
Zaman et al. [17]	1.Cationic surfactant C_{12}TAB 2.NaCl 3.Silica nanoparticles	1.Viscosity vs. shear rate. 2.Storage (G') & loss modulus (G") vs. frequency.	1.Inks, nanocomposite material, coatings, advanced structural ceramics, cosmetics.
Tao et al. [19]	1.Na_2SO_4 2.polyether demulsifiers (MD-1-MD-2)	1.Loss modulus vs. demulsifier concentration. 2.Dehydration ratio vs. dilational, elastic and loss modulus. 3.Demulsification speed vs. loss modulus. 4.Interfacial tension vs. Time	1.Deemulsification of crude oil emulsion in the petroleum industry.
Benjamin et al. [20]	1.Proteins- β - lactoglobulin, β - casein, ovalbumin and bovine serum albumin.	1.Modulus vs. time 2.Modulus vs. interfacial pressure	1.Microemulsion formation
Radulova et al. [36]	1.Hydrophobin 2.Lysozymes	1.Shear stress vs. time	1.Immobilization of functional molecules

	3.β-casein 4.asphaltene	2.Shear viscosity vs. rate of strain 3.Storage & loss modulus vs. rate of strain amplitude.	at surfaces. 2.Coating agents for surface modification.
Hooghten et al. [37]	1.Carbon black	1.Surface pressure vs. area 2.Storage and loss modulus with varying amplitude and frequency.	1.To prepare microscopically stable emulsion.
Seta et al. [38]	1.Non-ionic surfactant Tween 60 2.Anionic Admul DATEM 3.Ovalbumin protein	1.Interfacial tension studies at oil/water interface in presence of ovalbumin, tween 60 and admul. 2.Diffusion studies. 3.Storage modulus vs. angular frequency.	1.Food industry
Pang et al. [39]	1.Cationic emulsifier SBT 2.Non-ionic surfactant tween 80	1.Interfacial tension 2.Elastic modulus vs. surfactant concentration.	1. Asphalt emulsion production for slow set slurry surfacing, tack coat, fog seal etc.
Lakatos et al.[40]	1.Non-ionic surfactants ethoxylatednonyl-phenols $NPEO_{10-40}$	1.Viscosity vs. shear rate at different concentrations.	1.Enhanced oil recovery.
Lakatos-szabo et al. [41]	1.Sodium hydroxide	1.Viscosity vs. shear rate	1.Enhanced oil recovery.
Ge et al. [42]	1.Sodium linoleate 2.Linoleic acid	1.XRD pattern study 2.TEM	1.Microemulsion formation

Alvarez et al. [25]	1.Silica nanoparticles 2.NaCl 3.PDMAEMA homopolymer	1.Surface tension vs. time. 2.Dilational modulus vs. viscosity.	1.Formation of pickering nanoemulsion.
Ghosh et al. [15]	1.Cationic surfactant HTAB 2.NaCl, $CaCl_2$, $AlCl_3$	1.Interfacial tension 2.Viscosity vs. strain	1.Water and sewage treatment 2.Food 3.Material processing 4.Petroleum production 5.Textile, cosmetics and pharmaceutical industry.
Rane et al. [43]	1.Asphaltene 2.NaCl 3.$CaCl_2$	1.Elastic modulus vs. strain,time and frequency. 2.Interfacial tension 3.Viscous modulus vs. interfacial tension.	1.Enhanced oil recovey.

Interfacial tension imparts a major role in enhancing the rheology and to get a stable oil/water interface. Numerous previous research works has been carried out on interfacial tension reduction along with rheology at the oil/water interface. Tao et al. [19] studied both equilibrium and dynamic interfacial tension with respect to time and demulsifier performance for demulsification of crude oil and the subsequent results reveals the fact that both equilibrium and dynamic interfacial tension exhibited poor correlation with the demulsifier performance. Dilatonal modulus studies showed effective breaking of emulsion at dilational value of ~6mN/m. the crude oil/water emulsion validated elevated dehydration ratio at <5mM/m of elastic modulus. Previous studies cited by Tao et al. inveterate the fact that the steadiness of emulsion is mainly affected by the elasticity of the film. They also established some important facts about loss modulus and its direct variation with surfactant. Lower the

surface viscosity more it will promote the dispersal and arrangement of demulsifier at the interface. Seta et al. [38] demonstrated the adsorption of ovalbumin in presence of non-ionic surfactant Tween 60 and anionic Admul at the oil/water interface. They observed the interfacial tension is constant at low concentration of additives and consequently decreased up to a certain value where surfactant concentration is saturated. The interface with adsorbed protein layer has higher modulus and at high frequency and with the addition of surfactant viscoelasticity increases. Similar study done by Pang et al. [39] detailed the fact that at higher concentration of mixed surfactant system contributes to decrease in interfacial tension, also they stated that the increase in dilational modulus with increasing frequency may be due to substitution of surfactant monomers from bulk solution to the interface and may be due to conformational changes of surfactants at the oil/water interface. It is proved that nanoparticles can improve the interfacial rheology of liquid-liquid system, henceforth many experimental and simulation investigations has been done using nanoparticles as an additive along with surfactant and polymers. Alvarez et al. [25] used 20nm silica nanoparticles along with electrolyte and polymer. They found unmodified silica particle has no effect on interfacial tension and polymer grafted silica particle significantly reduces the interfacial tension. Their resultsimply that dilational modulus elevate the elasticity. Despite of these results dilational modulus study failed to explain the breakdown of homopolymer stabilized nanoemulsion after a certain time period. Ghosh et al. [15] studied the emulsion stability and interfacial rheology in the presence of different electrolytes and found that addition of electrolyte enhances the interface properties as it helps in interfacial tension reduction but with excess addition of electrolyte the repulsion between the droplets decreases and they start to coalescence resulting unstable interface. Dilational and shear rheological properties of oppositely charged polymer with cationic surfactant adsorbed at air/water interface has been investigated by Monteux et al. [44]. The adsorbed layer showed viscoelasticity and the degree of viscoelasticity varies with varied ratio of polymer and surfactant.

The surface tension/interfacial tension plays very critical role in both solubilization and rheological study for interface stability. So study of surface tension or CMC has been carried out by many researchers described in next section.

2.3 Previous studies on CMC of surfactants

The surface tension study of cationic and non-ionic surfactants has been carried out by Desai et al. [45]and Javadian et al. [46]. The results obtained explain that the CMC of single

surfactants is influenced to a greater extent when mixed with another surfactant. Javadian et al. [46] taken up an experimental investigation to study the effect of electrolyte, co-surfactants on the CMC and surface tension of pure surfactants. To reduce the environmental impact of surfactants, its production cost and to make stable system which are at first thermodynamically unstable many additives are used to enhance the potential of surfactant for solubilization as well as rheological parameters.

However, there is no such satisfactory justifications has been found till date regarding rheology at the air, oil/water interface and very less literature is available as compared with bulk rheology of interface. Henceforth, this research work is highlighting the shear and oscillatory rheology at the interface in presence of different additive.

3 OBJECTIVES

This chapter gives deals with the gap areas in literature which have been taken up in the current research. The salient features of the present work, has been presented in this chapter.

PAHs (napthelene, anthracene, phenanthrene, pyrene) are aromatic ring constituting only carbon and hydrogen and are wide spread in the environment arising naturally and also from man made products. It can be generated or found in forest fires, coal tar spillage, petroleum spillage, industrial waste etc. contaminating soil and ground water. In order to remove these toxic substances from our environment, solubilization of PAHs by surfactant enhanced remediation process has been taken up for this study among all the application of solubilization.

From the literature surveys it is clear that although many research works has been carried out with electrolytes to enhance the solubilization by surfactant but there is no such study showing the importance of higher valence electrolyte to reduce the consumption of surfactant to a greater extent to have a desired solubilization of PAHs. This study has focused on solubilization of anthracene and naphthalene by cationic surfactant CTAB with three different increased valence electrolytes NaCl, $CaCl_2$, Na_2SO_4.Cationic surfactanthas been chosen because it is best suited with electrolytes and CTAB along with electrolyte gives lower CMC. Sodium salts are used because these are cheap and does not have any adverse effect on environment. Reducing the consumption of surfactants with the application of electrolytes is both economical and environment friendly.

Our final aim is to have better solubilization of a substance in aqueous medium which initially is not soluble in water. In order to have better solubilization stability studies by rheological parameter measurements have been carried out at air, oil/water interfaces. Rheology studies at air/water interface has been carried out in order to observe the effect of cationic single chain surfactant CTAB, cationic double chain surfactant DDAB, non-ionic surfactant IGEPAL CO 630 on the stability at the interface. Attempt has been taken to reduce the surfactant composition by incorporating mixture of surfactant. To study the effect of electrolyte on stability of surfactant added air/water interface oscillatory and shear rheology investigations has been taken up with CTAB because cationic surfactant go well with electrolytes and among DDAB and CTAB, the later one is cheaper. The study has been

extended further to examine the effect of nanoparticle TiO_2 surfactant adsorbed oil/water interface. TiO_2 has been chosen on account of its wide applications in cosmetics, pharmaceuticals and as coating agent. TiO_2has positively charged surface, consequently anionic surfactant has been chosen with the prospect of synergism. SDBS has been chosen because of its lower CMC value among some of conventionally used anionic surfactant.

So the key purpose of the current research is to reduce the consumption of costly and toxic surfactants with the addition of electrolyte, nanoparticle and by incorporating surfactant mixtures to get optimum solubilization and stability.

4 EFFECT OF ELECTROLYTE ON PAHs SOLUBILIZATION IN CTAB MICELLAR SOLUTION

This chapter describes the experimental investigation of solubilization of anthracene and naphthalene in aqueous media with the help of cationic surfactant CTAB. Effect of three different electrolytes of increased valency NaCl, $CaCl_2$, Na_2SO_4on solubilization of CTAB has been studied. A comparison has been done between the superiority of electrolyte added system with pure CTAB. The investigated results have again been justified with 1D ^1H NMR study.

4.1 Introduction

Addition of neutral electrolyte to ionic surfactants accounts for the enhanced solubilization. Small concentration of electrolyte helps in hydrophobic interaction reduces the CMC, hence aggregation number of micelles increases. From the literature sodium salts are the second best electrolytes to be used with ionic surfactants for enhanced solubilization [47]. In addition to that these are not harmful to ecosystem and cheap. $CaCl_2$ has been used in order to show the effect of increase in co-ions in solubilization and to compare it with increase in counterion.

4.2 Materials

The surfactant CTAB (~99% purity) was purchased from Sigma Aldrich, Germany. Other chemicals such as naphthalene (98%, SpectrochemPvt. Ltd.), anthracene (99%, LobaChemie),NaCl (99.9%, Rankem), $CaCl_2$ (99.5%, Merck) and Na_2SO_4 (98%, Merck) were used as received. Ultrapure waterwas used for the experiments of 18.2 mΩ resistivity and pH 6.8-7 excluding ^1H NMR which uses D_2O (99.9%, Sigma aldrich). CMC of surfactant has been determined by surface tensiometer (Dataphysics, DCAT11EC). Concentrations of PAHs were measured by a UV-Vis spectrophotometer (Shimadzu, Japan, UV-3600). The 1D ^1H NMR experiment was done by Bruker Ultrashield 400.

4.2.1 Properties of surfactant used

CTAB

Cetyltrimethylammonium bromide is a cationic single chain surfactant with molecular weight of 364.46g/mol and has a molecular formula $(C_{16}H_{33})N(CH_3)_3Br$. It is water soluble

surfactant and this go well with electrolytes. It has molecular structure as shown in Fig.4.1. The CMC value for CTAB is 0.9-1mM/L.

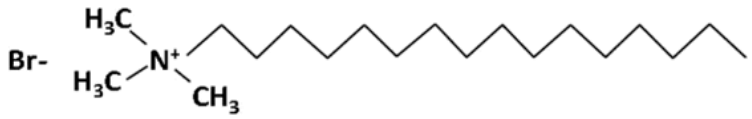


Fig. 4.1: CTAB structure.

4.3 Experimental Methods

4.3.1 Surface tension measurement

Surface tension measurements were done with a surface tensiometer by platinum wilhelmy plate method.A stock solution of surfactant was prepared by dissolving it with ultrapure water and from that, varying concentrations of surfactant were taken and diluted with ultrapure water and surface tension was measured with increasing concentration of surfactant. The surface tension values were plotted against surfactant concentration to get the CMC curve. The working formula for wilhelmy plate tensiometer is given by [48]

$$\gamma = \frac{F}{l\cos(\theta)} \qquad (4.1)$$

Where γ = surface tension (mN/m)

F= the magnitude of the capillary force on the plate due to wetting.

l = the wetted perimeter ($2w + 2d$)

w= plate width, d =plate thickness

θ= contact angle between the liquid phase and plate

4.3.2 SolubilizationMeasurement

All the solubilization experiments were done in the polypropylene falcon tubes of capacity 15mL. The stock solutions of naphthalene (400mM) and anthracene (4mM) were prepared by dissolving them in pure methanol. Methanol has been preferred over higher alcohols because of its negligible effect on solubilization and CMC values. For the solubilization experiment, 0.1 mL of PAH from the stock was added to 10 mL of surfactant solution. The concentration and volume of the stock PAH solution used in each experiment was selected to (i) keep the methanol concentration in the test solution below 1 % by volume, and (ii) to give an excess of

PAH in the test solution. The tube was sealed with a screw cap to prevent volatilization of PAH from water. For the solubilization study, 24 h equilibration time was considered, as there was almost no change in solubility of PAHs found from the kinetics study. After the equilibration period, the mixture was centrifuged at 12000 rpm for 15 min to separate the suspended solids, if any. The concentration of naphthalene and anthracene were determined bymeasuring the absorbance at 275 and 375.5 nm wavelengthsrespectively using a UV-vis spectrophotometer. Meanwhile, subsequent dilutions were made wherever needed, and same concentration surfactant solution was keptinthe referencecell to minimize the effect of surfactant on UV absorbance. All experiments were performed at room temperature, 25-28℃. Experiments were done in triplicate to validate the reproducibility.

4.3.3 1D ^{1}HNMR Spectroscopy

NMR experiment was carried out at 298.2K. Samples containing 10mM of CTAB, CTAB with PAH and CTAB, PAH with electrolyte has been prepared to perform the experiment. PAH was added in excess amount. The samples were kept for 72 hour to attain maximum solubilization and then 1.7ml of sample taken from the sample bottle and centrifuged at 12000rpm for 15 min then 1ml of supernatant liquid is withdrawn to a 0.4cm NMR tube to perform the experiment. The NMR experiment of pure CTAB was performed right after the solution preparation. All the solutions were prepared by dissolving them in D_2O.

4.4 Results and discussion

4.4.1 Surface tension study of CTAB solution

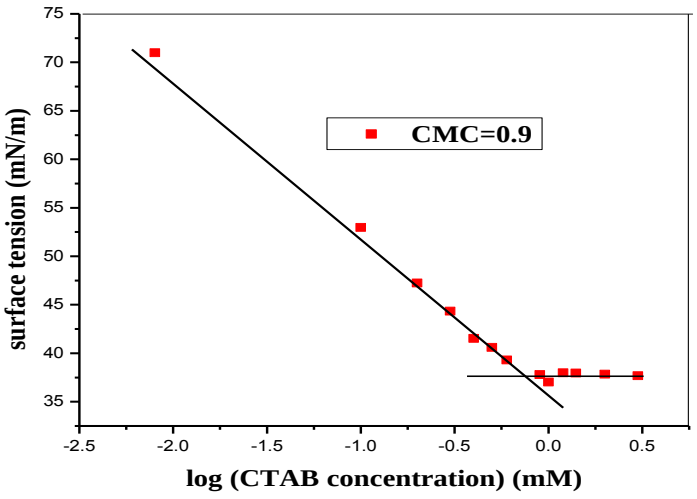
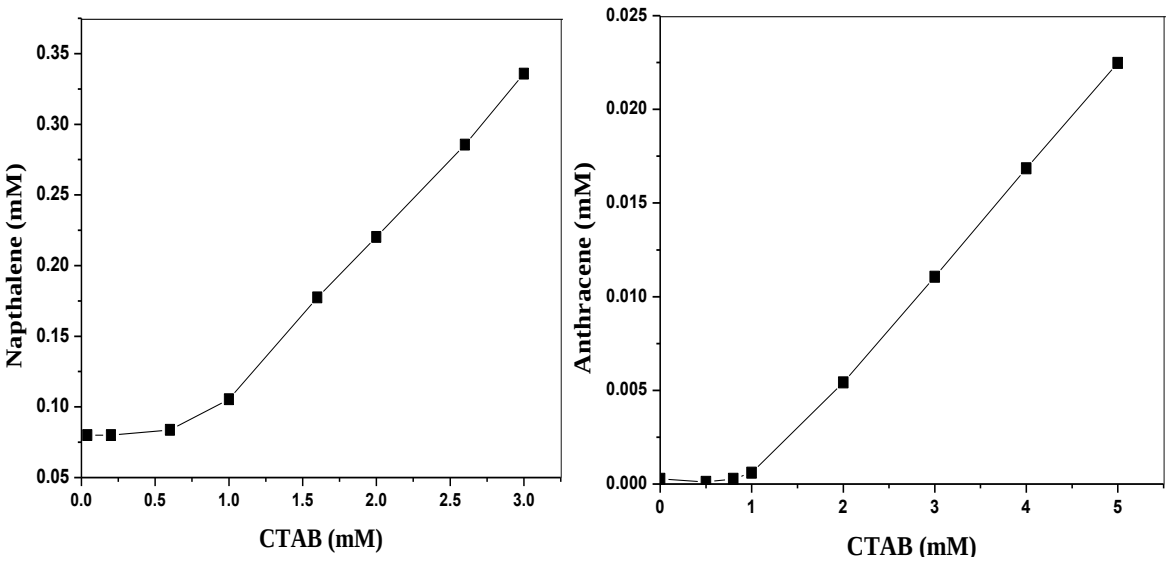


Fig.4.2:surface tension vs. surfactant concentration.

From Fig.4.2, it can be concluded that addition of surfactant greatly reduces the surface tension of water. Water has a high surface tension of 71.97millinewton/meter at 25 °C and it reduces to approximately 37millinewton/meter, when we add surfactant of 1-3mM concentration. When we add surfactant it adheres to the water surface and reduces its surface energy required to increase the surface area of water molecules, hence surface tension decreases. On further addition of surfactant above CMC no change in surface tension occurs.

4.4.2 Solubilization of PAHs in pure CTAB solution

Cationic surfactants exhibit greater solubilization efficacy of PAHs due to adsorption at micellar water interface in addition to solubilization in the inner core of micelle[29].Additionally, unlike anionic surfactants, the cationic surfactants are stable in the presence of electrolytes without precipitating from the solution. Because of these reasons a cationic surfactant was chosen to study the solubilization behavior. The changes in solubility of both PAHs with the increasing concentration of surfactant are presented in Fig.4.3. As expected, below the CMC of the surfactant there is no change in solubilization, but increases linearly with the increase in surfactant concentration above CMC. The CMC we got from surface tension study is 0.9mM and from the solubilization of naphthalene and anthracene the CMC of CTAB was found to be 0.9mM and 1mM respectively. So it can be inferred that solubilization studies are as illustrious as surface tension studies to find out CMC.



(a) (b)

Fig. 4.3: Solubilization of (a) naphthalene (b) anthracene by pure CTAB solution.

The molar solubilization ratio (MSR) is the parameter generally used to quantify the potency of solubilization of a surfactant, which can be defined as the moles of organic compound solubilized per mole of micellized surfactant. The MSR can be determined as

$$MSR = (S - S_{CMC}) / (C_S - CMC) \qquad (4.2)$$

where, S is the apparent solubility of organic compounds at surfactant concentration C_S (C_S> CMC) and S_{CMC} is the apparent solubility of the organic compounds at the CMC. It can alsobe determinedby the slope of linearly fitted line of solute concentration vs. surfactant concentration curve, above CMC.

Whereas, partitioning of the organic compounds between micelles and monomeric solution is an alternative approach in quantifying the surfactant solubilization. The micellar-water partition coefficient (K_m) is another parameter that based on the mole fraction ratios, the ratio of mole fraction of the compound in the micellar pseudophase (X_m) to the mole fraction of the compound in the aqueous pseudo phase (X_a) and can be expressed as

$$K_m = X_m / X_a \qquad (4.3)$$

where, the value of X_m can be calculated as X_m = MSR/(1 + MSR), and X_a as $X_a = S_{CMC}V_w$, where, molar volume of water, V_w = 0.018 07 L/mol [2]. All the MSR and K_m values are tabulated in Table4.1. From the MSR and Log (K_m) values, anthracene has very low solubility in comparison with naphthalene as triple ringed aromatic compound anthracene has higher molecular weight than double ringed naphthalene. However solubility in pure water increases to a greater extent with the addition of surfactant.

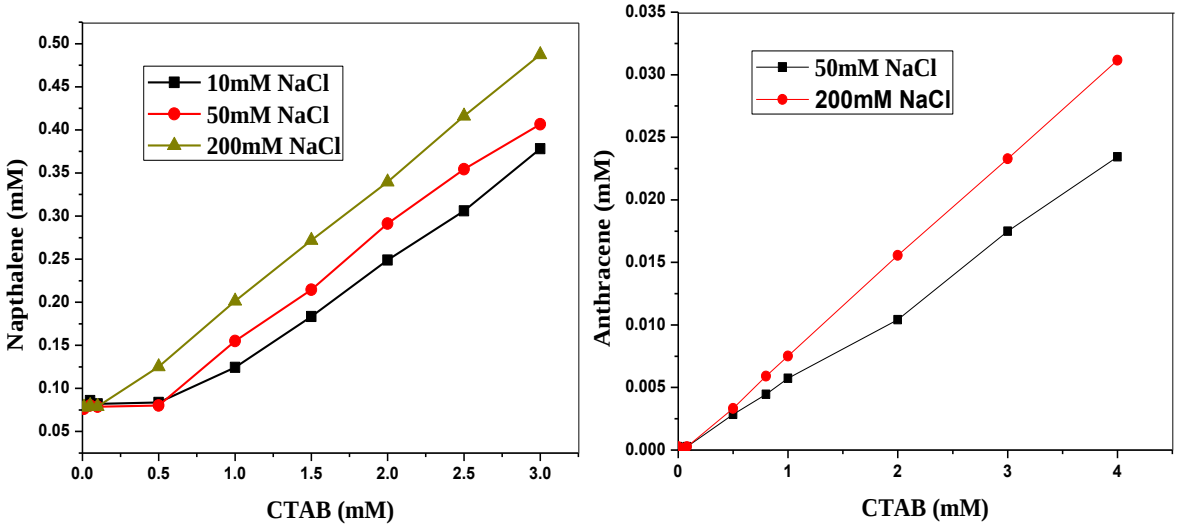
4.4.3 Effect of electrolytes on solubilization of PAHs with CTAB

The solubilization activity ofnaphthaleneand anthracene in the presence of different electrolyteshas been studied to check the augmented effectiveness over contamination concerns, commercially as well as environmentally.Hence, to determine the efficacy of electrolyte for extended applicability,solubilization in pure CTAB has beencarried out initiallybefore studying the solubilization behavior of naphthalene and anthracene with different electrolytes.

The influence of three different electrolytes NaCl (1:1), Na_2SO_4 (1:2) and $CaCl_2$ (2:1) on solubilization of PAHs was studied in the presence of cationic surfactant (CTAB).The cationic surfactant shows enhanced solubilization proficiency for PAHs than other ionic surfactants [2]may be due to adsorption at micellar-water periphery in addition to solubilization at inner core of micelle.In the presence of electrolytes, CMC was reached at concentration far below that of the original CMC, depending on the concentration of the

electrolytes. Since surfactant molecules adsorbed at the water PAH interface, after adding electrolytes lateral interactions between tail group (hydrophobic bonding) increases whereas electrical repulsion between similar charged head groups is weakened due to the presence of counterions.According to the Schulze-Hardy rule, the charge screening efficiency or the ability to reduce the Debye length of a multivalence ion is comparatively greater than that of monovalence ion, hence,multivalence salt requirement is significantly less than monovalence to acquire similar value of surface tension at reduced CMC and enhanced solubilization. When we add electrolytes in small concentrations to the surfactant solution, the solution becomes more thermodynamically stable and hence further decrease in interfacial tension can be observed as the energy required to increase the surface area is lowered, hence, solubilization of PAHs becomes more significant [33].

4.4.3.1 Effect of NaCl (1:1) on solubilization of PAHs



(a) (b)

Fig. 4.4: Solubilization of (a) naphthalene and (b) anthracene using CTAB with different NaCl concentrations.

The effect of constant NaCl concentration has been studied over the PAH solubilization efficiency with varying surfactant concentration. Fig. 4.4 and Table 4.1 illustrates that, with increasing concentration of NaCl, the slope of solubilization curve (MSR) & Log (K_m) values increases, which implies that with increasing concentration of NaCl the solubilization capacity of CTAB increases. In the present study, for 50mM NaCl solution, the CMC of CTAB reduces from 0.9mM to 0.5mM and naphthalene solubilization enhances to 32.28% as compared to solubilization in pure CTAB solution. Similar event observed for anthracene as

the solubilization increases from 0.005421mM/L to 0.010409mM/L at 2 CMC with the addition of 50mM NaCl. When we add NaCl salt in cationic surfactant solution, Cl^- mitigates the head group repulsion as well as the hydrophilic solubilization, thus amplify the lipophilic or hydrocarbon-hydrocarbon interaction instigating enhancement in solubilization [31].This can be attributed to the fact that at a very low surfactant concentration with electrolyte, the surfactant cation and counteranion are fully dissociated and reaches to a plateau level upto the CMC and, above CMC, the solubilization of PAHs initiated. CMC was reduced far from the original setting the fact that we can achieve the desired reduced surface tension at a very low surfactant concentration with the addition of electrolyte.

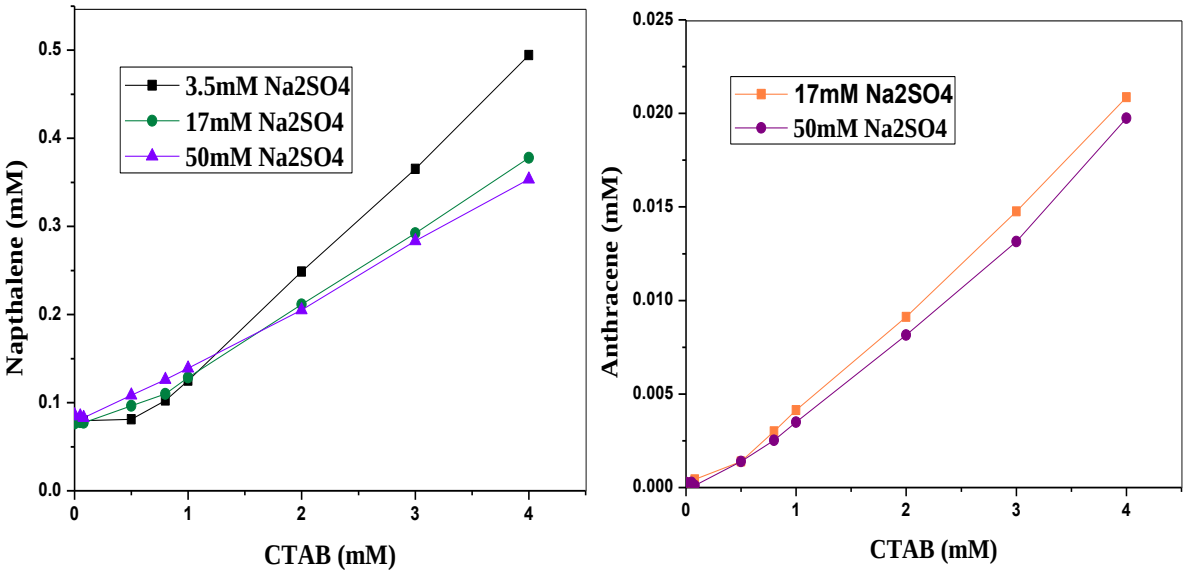
Table 4.1: Values of CMC, MSR and log K_m for different systems.

	Napthalene			Anthracene		
	CMC (mM)	MSR	Log(K_m)	CMC	MSR	Log(K_m)
CTAB	0.9	0.1138	4.85	1	0.0055	6.047
CTAB+10mM NaCl	0.7	0.126	4.87	–	–	–
CTAB+50mM NaCl	0.5	0.1318	4.91	0.5	0.0059	6.173
CTAB+200mM NaCl	0.1	0.142	4.94	0.1	0.0079	6.298
CTAB+3.5mM Na_2SO_4	0.62	0.122	5.156	–	–	–
CTAB+17mM Na_2SO_4	0.4	0.0817	4.734	0.4	0.0055	6.047
CTAB+50mM Na_2SO_4	0.2	0.0708	4.637	0.2	0.0052	6.023
CTAB+4mM $CaCl_2$	–	–	–	0.62	0.0051	5.356
CTAB+10mM $CaCl_2$	–	–	–	0.59	0.0053	5.32
CTAB+16mM $CaCl_2$	–	–	–	0.5	0.0052	5.11

The depression of CMC with increasing electrolyte concentration may be due to the decrease in thickness of ionic atmosphere surrounding the ionic headgroups and the consequent decreased repulsion between them in the micelle.

4.4.3.2 Effect of Na_2SO_4 (1:2) on solubilization of PAHs

Bivalent counterion (SO_4^{2-}) requires very less electrolyte concentration to attain the same ionic strength as compared to monovalent (Cl^-) counterion as well as reduces the surfactant concentration. Fig. 4.5 illustrates the effect of constantNa_2SO_4 over naphthalene and anthracene solubilization efficiency with varying surfactant concentration. With the addition of 3.5mM $Na_2SO_4$to 2mM of CTAB, solubilization of naphthalene reaches to 0.248732mM/L from 0.22023mM/L with pure CTAB which is nearly equal to the solubilization with 10mM NaCl.



(a) (b)

Fig. 4.5: Solubilization of (a) naphthalene and (b) anthracene using CTAB with different Na_2SO_4 concentrations.

The effective counter ion charge density is high for the higher valence ions, henceforth; electrolytes with higher valency are more effective to screen the charge of the surfactant head groups. Due to the presence of more number of counter ions the micellar size becomes denser with a bigger size; hence micellar core is able to accommodate more hydrophobic compounds.Ionic strength plays a crucial role to enhance the solubility of PAHs; meanwhile, the valency of the counter-ion is another important factor to enhance the solubilization as well as partition coefficient between micellar and aqueous phase. With increasing valency of electrolytes the surfactant consumption can be reduced to achieve the desired solubilization

with very less concentration of electrolytes. But with high concentration of bivalent electrolyte the solubilization starts to decline as with much high concentration of Na_2SO_4 entire micelle may covered with only electrolyte and possibly there is no room for PAH to get inside the micellar core for solubilization. Another possible reason for decrease in solubilization could be stated as, with much higher concentration of bivalent electrolyte the anionic PAH maybe repelled strongly by the electrolyte subsequently there is less or no diffusion of PAHs from aqueous phase to micellar phase, resulting in decrease in partition coefficient as number of molecules of PAH is more in aqueous phase than in micellar phase. From Fig. 4.5: the solubilization of anthracene is also declining after certain increase in Na_2SO_4concentration.

4.4.3.3 Effect of $CaCl_2$ (2:1) on solubilization of PAH

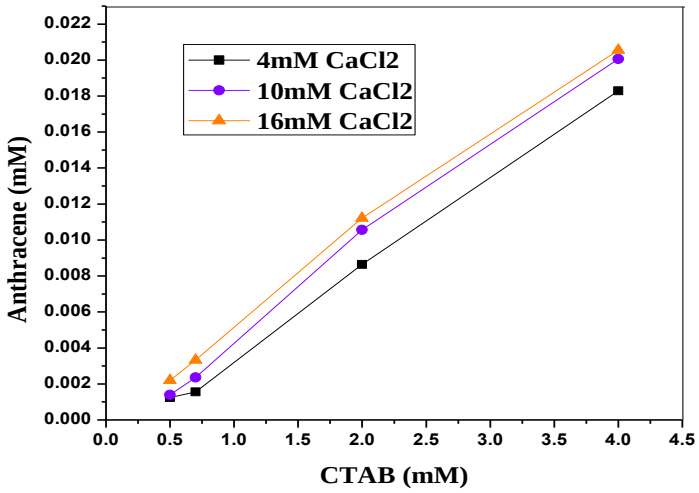


Fig. 4.6: Solubilization of anthracene using CTAB with different $CaCl_2$ concentrations.

Solubilization experiment of anthracene by CTAB along with $CaCl_2$has been carried out (Fig. 4.6)to study the effect of co-ions on PAH solubilization. With increasing concentration of $CaCl_2$ electrolyte, there is no enhancement of solubilization happens as compared to pristine cationic surfactant CTAB, NaCl and Na_2SO_4, whereas it has been observed thatdue to thepresence of higher valence co-ions in $CaCl_2$, solubilization diminishes.MSR and Log (K_m) values are less than pure CTAB and gradually reduces with increasing concentration of $CaCl_2$. It has to notify that, though the CMC using$CaCl_2$ is reducing to nearly same value of Na_2SO_4 but solubilization of organic contaminants is not significant comparatively. This can be attributed to the fact that co-ion is less significant to enhance the solubilization as it increases the head group repulsion for cationic surfactant. On the other hand, counterion reduces the electrical double layer thickness around the surfactant heads, which reduces the

repulsion between two adsorbed surfactant molecules. One possible explanation may be that cationic surfactant favors the electrostatic attraction with counterions to enhance the solubilization.

4.4.4 Comparison of different electrolytes with ionic strength:

Further investigation has been carried out to quantify the naphthalene and anthracene solubilization efficiency of three different electrolytes NaCl (1:1), Na_2SO_4 (1:2) and $CaCl_2$ (2:1) with varying CTAB concentrations. The consumption of bivalence counterion (SO_4^{2-}) electrolyte is far less as compared to monovalence (Cl^-) counterion , and in addition to that it reduces the consumption of surfactants mainly by reducing CMC as well as increasing the MSR and log K_m values. Fig. 4.7 (for 2mM CTAB) demonstrates with increasing ionic strength of NaCl, naphthalene & anthracene solubilization increases significantly but with increasing ionic strength of higher valence electrolytes the solubilization diminishes as described earlier in this paper. For $CaCl_2$ with increasing co-ions there is no such significant enhancement happens. Another perceptible fact that can be extracted from ionic strength data is to get 100mM of ionic strength we need 200mM NaCl, whereas 50mM Na_2SO_4 is giving the same ionic strength. Hence, it justifies that, the requirement of higher valence electrolyte is much lower as compared to less valence electrolyteto get higher ionic strength and we can validate the fact that use of higher valence electrolyte reduces the surfactant consumption to a greater extent. From experimental results it can be interpreted that solubilization efficiency of naphthalene and anthracene with $CaCl_2$ is less significant as compared to NaCl and far much lower than higher valence electrolytes. This can be attributed to the fact that co-ion is less significant to enhance the solubilization with CTAB due to the reduction in the potential of PAHs extraction at the soil surface.

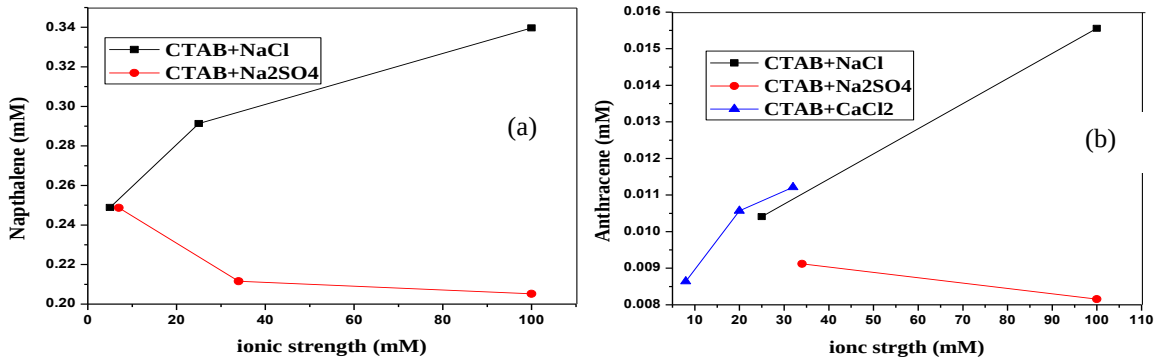


Fig. 4.7: (a) Naphthalene (b) anthracene solubilization with increasing ionic strength of different electrolytes.

4.4.5 1D ^{1}H NMR Experiment:

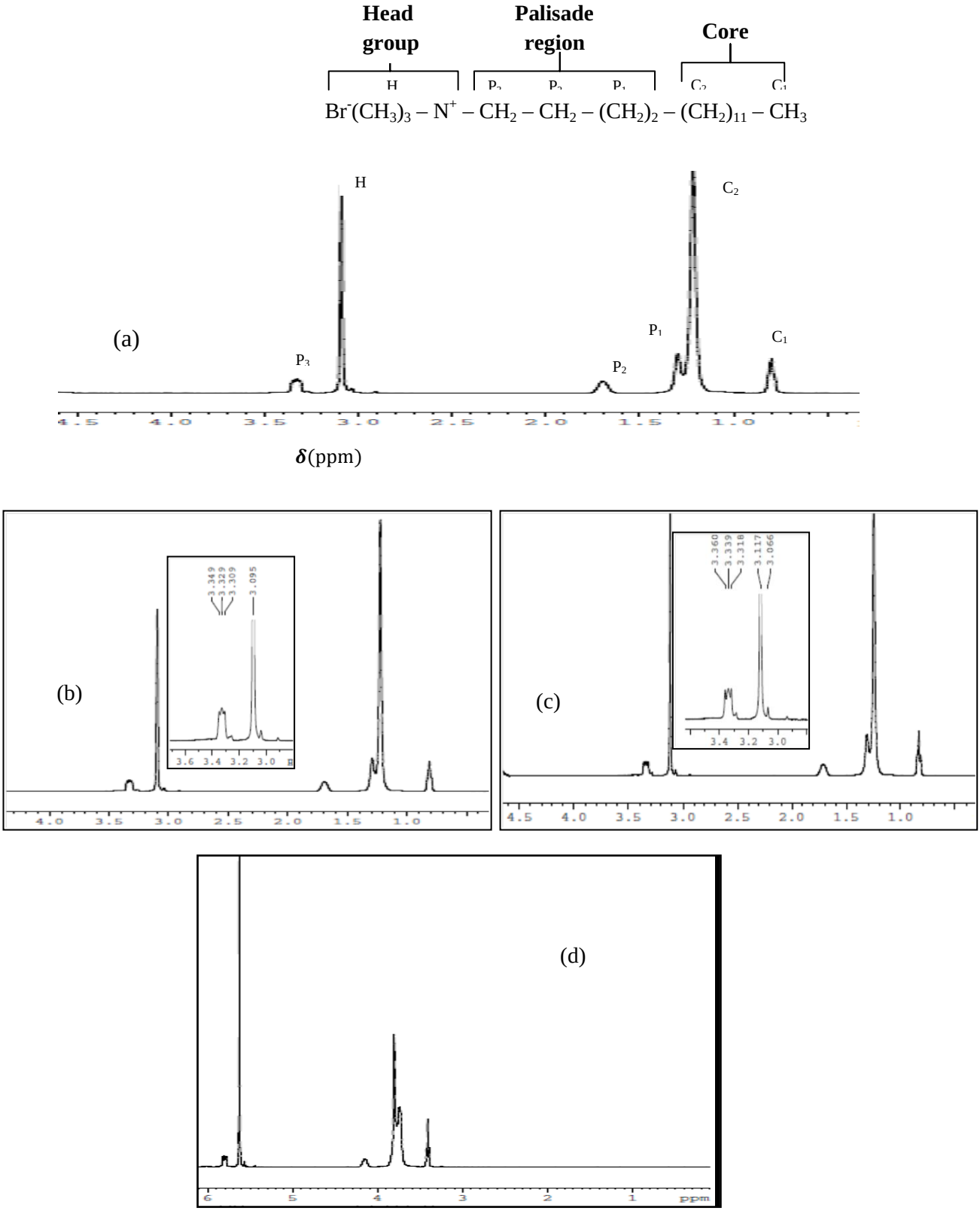


Fig.4.8: ^{1}H NMR spectrum for (a) 10mM pure CTAB, (b) CTAB with anthracene, (c) CTAB, anthracene along with NaCl, (d) CTAB, naphthalene along with NaCl.

1D ^{1}H NMR data shows the peaks at different $\boldsymbol{\delta}$(ppm)illustratingthe position of hydrogen (proton) at different region on CTAB molecules in the micelles. The peak values and chemical shifting of peaks are tabulated in Table 4.2. Fig. 4.8: (a) represents the 1H NMR spectrum of pure CTAB and the results and peaks obtained are quite similar to the previous studies [49, 50]. When we are solubilizing PAH with the help of surfactant (Fig. 4.8: (b)), upfield shifting is pronounced. As from table-2 after incorporating anthracene peaks P_1, P_2 and P_3 undergoes upfield shifting implying the solubilization of anthracene is prominent inside the palisade region with reference to other regions of CTAB micelles.

Table 4.2: ^{1}H chemical shift data for different solutions.

Solutions	Peaks					
	C_1	C_2	P_1	P_2	P_3	H
CTAB	0.798	1.218	1.298	1.698	3.351	3.091
CTAB+ Anthracene	0.811	1.223	1.290	1.692	3.349	3.095
CTAB+ Anthracene+ NaCl	0.833	1.246	1.309	1.710	3.36	3.117
CTAB+ Napthalene+ NaCl	3.413	3.746	3.806	4.148	5.803	5.626

The possible explanation for this shielding effect may be in the palisade region electronegetivity is reduced due to the addition of electron density. Smaller upfield shifting was observed may be due to inefficient shielding effect on hydrogen [51]. NaCl addition instigates the Cl^- ion to help in reducing the e^- density at the micellar surrounding and the nucleus happens to be in the vicinity of electronegetivity and the protons are deshielded in the micelle resulting in downfield shifting of the peaks. However, NMR results can only envisage the vicinity of a functional group that contains hydrogen. Fig. 4.8: (d) represents the naphthalene solubilization in CTAB solution in presence of NaCl. The shifting of peaks is larger than anthracene as justified by Table 4.2 illustrating higher solubilization of naphthalene over anthracene.

5 STABILITY STUDY BY RHEOLOGICAL MEASUREMENTS: EFFECT OF ADSORBED SURFACTANT MIXTURES AT AIR/WATER INTERFACE

Present chapter addresses the issue of stability when we are dealing with two immiscible substances with the addition of surfactants and surfactant mixtures. Surface tension of cationic (single chain CTAB, double chain DDAB) and non-ionic (IGEPAL CO 630) surfactants and of their mixture (DDAB & IGEPAL CO 630) is investigated followed by to check the stability experiments were conducted using shear and oscillatory rheology techniques. The effect of added surfactant and their mixture on surface tension reduction to enhance the shear & oscillatory parameters has been emphasizedto facilitate a stable air/water interface.

5.1 Introduction

The study of rheology at the surfactant adsorbed interface describes the stability of the system and understanding that will lead to a better solubilization of insoluble materials. Rheological study describes the flow behavior of surfactant solutions so that the surfactants can be categorized for different applications. Storage (G') & loss (G") modulus describes the viscoelastic nature of the surfactant solution. Mixture of different types of surfactant frequently shows synergistic effect. This property of surfactant makes them functionalfor many industrial applications. They are used to reduce the air/liquid or liquid/liquid interfacial tension. A study on adsorption of pure surfactants and interaction between adsorbed surfactant mixtures helps in a lucid way to select a surfactant or combination of surfactant for optimum properties[1].

This study has beentaken up to find out best possible surfactant or surfactant mixtures to reduce the surface tension at air/water interface for practical applications in food, paint, enhanced oil recovery, pharmaceutical and cosmetics industry. The surface tension studies of single chain cationic surfactant CTAB, double chain cationic surfactant DDAB and non-ionic surfactant IGEPAL CO 630. Also the surface tension study of surfactant mixtures (DDAB+IGEPAL CO 630) has also been studied. The rheology of micellar solution of these surfactants with water has also been carried out to predict the flow and oscillatory rheological properties.

5.2 Materials

CTAB used is same as described in previous chapter. Non-ionic surfactant IGEPAL CO-630 and double chain cationic surfactant DDAB were purchased from Sigma Aldrich. All the solution were prepared using ultrapure water (Sartorius, Germany) of 18.2MΩ·cm resistivity, 71.5 mN/m surface tension, and 6.5-7 Ph at 25 ± 0.5°C. For all the experiments, a single surfactant solution or mixture of surfactant solution of desired concentration was prepared by diluting a concentrated stock solution.

5.2.1 Properties of surfactants used

IGEPAL CO-630

Polyoxyetylene (9) nonylphenylether or IGEPAL CO 630 is a non-ionic surfactant with molecular weight of 617g/mol and has a molecular formula $(C_2 H_4O)_n \cdot C_{15}H_{24}O \cdot$ n=9-10. It is a water soluble surfactant. It has amolecular structure as shown in Fig. 5.1. The theoretical CMC of IGEPAL CO 630 is 0.05mM.

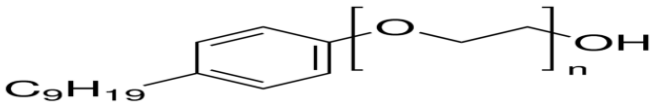


Fig. 5.1: IGEPAL CO 630 structure.

DDAB

Didodecyldimethylammonium Bromide is a double chain cationic surfactant with molecular weight of 462.63g/mol and molecular formula $C_{26}H_{56}BrN$. It is soluble in water and has tolerance for salts. It has a molecular structure as shown in Fig. 5.2. The CMC value for DDAB is 0.039mM. As it is double chain surfactant it also form vesicles and has a CVC of 0.79mM.

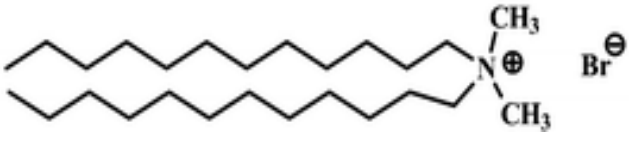


Fig. 5.2: DDAB structure.

5.3 Methods

5.3.1 Surface tension measurement

All the surface tension experiment methods are same as described in chapter 4.

5.3.2 Rheology experiments

All rheological measurements were performed by stress controlled TA HR-2 Discovery Hybrid Rheometer (Fig. 5.3). Generally this rheometer has different operating test mode like flow, ramp, and oscillation. In a different mode, we can perform different operations. Rheometer can be equipped with different geometries like cone and plate, parallel plate, concentric cylinder double gap cylinder and du-nouy ring. In this measurement du-nouy ring, geometry was used. Du-nouy ring is made up of platinum, has a thickness of 0.8mm having outer diameter of 19.8mm and inner diameter of 19.0mm.

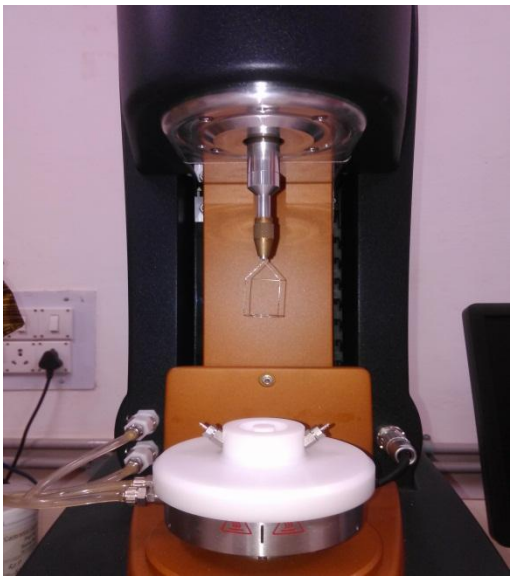


Fig. 5.3: Rheometer with Du Noüy ring geometry.

The du-nouy ring measures the rheological properties of the solution on the basis how molecules at the interface behaves on applied strain by rotational motion of the ring. Simultaneously it has drawback also because as it is very thin and costly we have to handle it very carefully. When liquid is placed on a trough the du-nouy ring comes down and basically when the ring is rotated, the force on solution measured. Ring dimensions and Rotationalspeed give the shear rate. This

rheological characterization includes the determination of relative viscosity and stress with respect to strain, effect of step time on viscosity, Oscillatory Rheology. All the experiments were carried out at 25˚C.

5.4 Results and discussion

5.4.1 Surface tension study of single surfactants

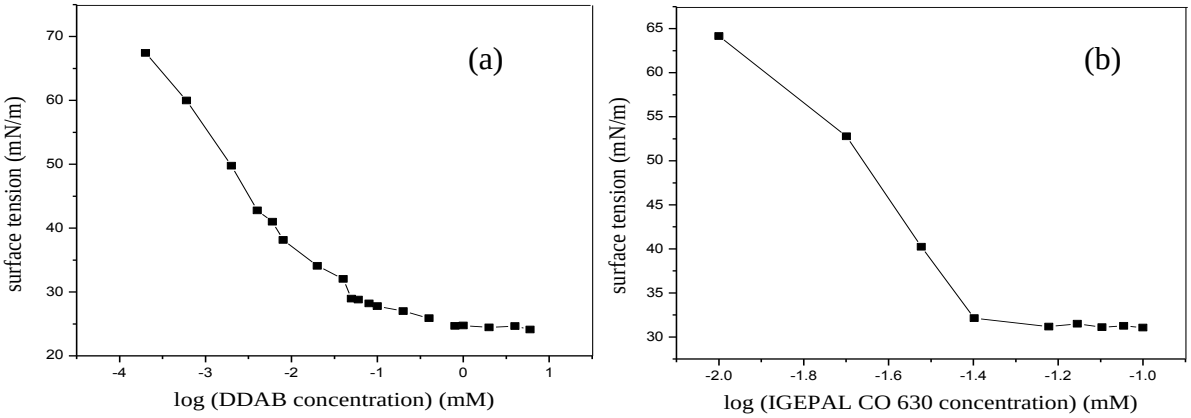


Fig. 5.4: Surface tension vs.(a) DDAB, (b) IGEPAL CO 630 concentration curve.

From Fig.5.4, the nature of surface tension reduction with addition of surfactant has same nature as described earlier. From the graph the CMC value for DDAB is 0.039mM & for IGEPAL CO 630 is 0.041mM and surface tension values at CMC obtained are 28.195mN/m and 32.5mN/m respectively. As DDAB is a double chain cationic surfactant, it possesses two hydrocarbon chain of same length. When we add DDAB to water it forms micelles and after a certain concentration it forms vesicles resulting bigger form of micelles and more reduced surface tension of water and has a CVC of 0.79mM. IGEPAL CO 630 is a non-ionic surfactant i.e. its head group does not possess any charge, but the hydrogen groups present in its head part forms hydrogen bond and helps in reducing water surface tension.

5.4.2 Surface tension study of DDAB & IGEPAL CO 630 mixed system

DDAB and IGEPAL CO 630 has been chosen to study the effect of mixed surfactant system because their CMC values are quite close to each other depicting the fact they possess similar type of surface properties. The concentration of these two surfactants varied in the ratio of

9.5:0.5, 9:1, 8:2, 7:3 and the studies has been carried out to find out the combination with optimum properties.

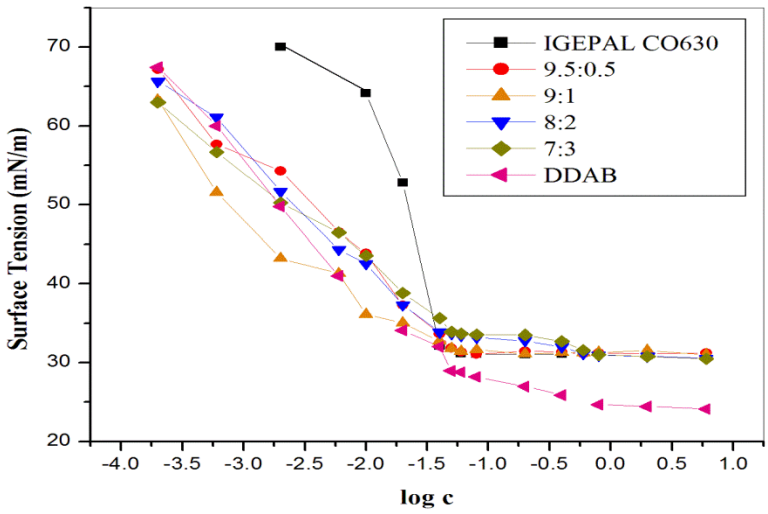


Fig. 5.5: The change in surface tension (mN/m) with the concentration (log c) of DDAB and IGEPAL CO 630 mixture at different ratio.

Surface tension of IGEPAL CO 630 is decreasing with the addition of increased concentration of DDAB as illustrated by Fig. 5.5 and Table 5.1. The two surfactants showed synergistic behavior at different varied concentrations as explained by the interaction parameter β calculated from equation (5.1) On the basis of Rubingh's [52] theory

$$\beta = \frac{\ln\left[\frac{C^*\alpha_1}{C_1 X_1}\right]}{(1-X_1)^2} \qquad (5.1)$$

Where X_1 is the mole fraction of surfactant 1 in a mixed micelle. C_1C_2 and $C_{12}$are the CMC of surfactants and their mixture. If two surfactants are mixed together, it's mixed CMC (C^*) values are given by the equation [53] (5.2)

$$\frac{1}{C^*} = \frac{\alpha_1}{f_{1C_1}} + \frac{(1-\alpha_1)}{f_2 C_2} \qquad (5.2)$$

Where α_1 isthe mole fraction of surfactant 1 in total mixed solute, $f1$ and $f2$ are the activity coefficients of surfactants 1 and 2, respectively, and $C1$ and $C2$ are the CMC of surfactants. In ideal case $f1= f2=1$; hence equation (5.2) becomes,

$$\frac{1}{C^*} = \frac{\alpha_1}{C_1} + \frac{(1-\alpha_1)}{C_2} \quad (5.3)$$

The more the negative is $\beta -$ parameter surface activity will be more and the surfactant solution helps in reducing ST in a more effective way. Among all the surfactant mixtures 8:2 ratio has proved to be the optimum one as its β-parameter is more negative. More negative is β-parameter the less will be the energy required to increase the surface area.

From the above surface tension studies, the data and graphs we have obtained, we can observe that DDAB is the most efficient surfactant in reducing ST. But as its very costly and to reduce its environmental crash we incorporate surfactant mixture system for optimum results.

Table 5.1: Values of surface tension, interaction parameter, critical micellar concentration (CMC) for pure and mixed surfactant solutions (DDAB + IGEPAL CO 630).

Mole fraction (IGEPAL CO 630)	**CMC (experimental) (mM)**	**CMC (Theoretical) (mM)**	**CVC (Experimental) (mM)**	**Interaction parameter (β)**	**Surface Tension (γ)**
1	0.039	-	-	-	32.5
0.95	0.0407	0.0409	-	-0.32154	31.872
0.9	0.0354	0.0408	-	-1.14978	31.765
0.8	0.0316	0.0406	0.446	-1.31119	30.521
0.7	0.0309	0.04	0.398	-1.18773	30.492
0	0.041	-	0.79	-	28.195

5.4.3 Shear & oscillatory rheology of surfactants

Rheological studies give the fundamentals on what is happening in molecular level, at the interface, how the flow and oscillatory behavior is affected by surfactants can be observed through rheological studies.

Stress & viscosity variation with strain & time

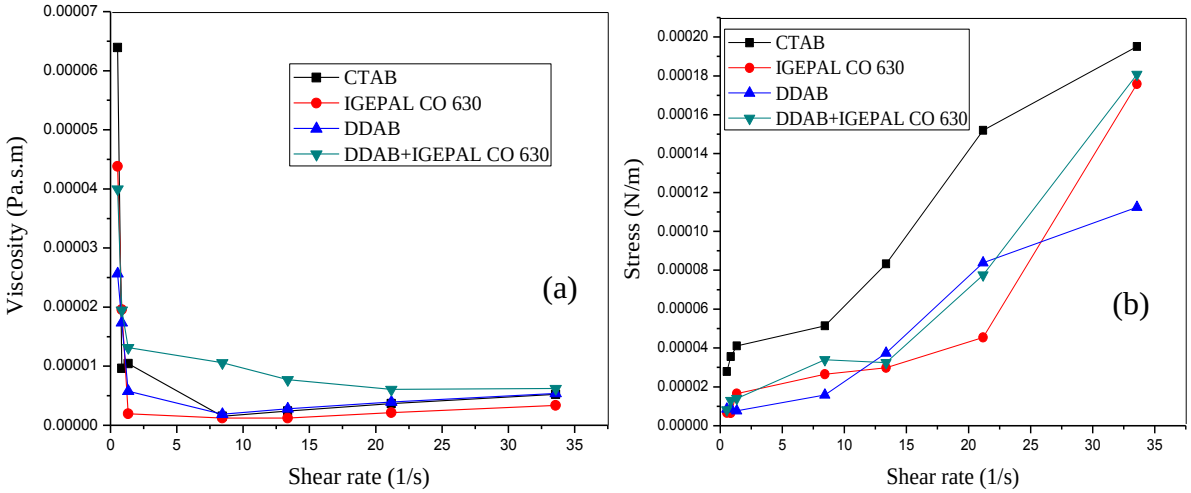


Fig. 5.6: Variation of (a) viscosity and (b) stress with strain at air/liquid interface in presence of different surfactant and their mixture.

The variation of viscosity with respect to both shear rate and different types of surfactants used at a concentration above CMC are shown in Fig. 5.6. Viscosity is decreasing with increasing shear rate depicting the fact that surfactant solutions are exhibiting non-newtonian shear thinning behavior. The reduced surface tension by surfactants also plays important role in viscosity reduction. Cationic single chain surfactant CTAB has highest surface tension among all the surfactants considered in this study with a value of 37mN/m and contributes to the highest viscosity. Table 5.2 & Fig. 5.7 (b) shows that viscosity has a direct variation with surface tension of micellar aqueous medium. The surfactant mixture system DDAB+IGEPAL CO 630 used at a ratio of 8:2 (optimized selection) shows a behavior nearly equal to IGEPAL CO 630 with a synergism may be due to the dominance of IGEPAL CO 630 concentration. All the viscosity curves are downgrading from a highest value and approaching towards a nearly single limiting viscosity value forming a plateau level above which no further reduction of viscosity happens.

According to Ostwald-de waele relationship

$$\tau \propto \frac{\partial u}{\partial y} \qquad (5.4)$$

i.e. increasing stress (applied force) contributes increase in fluid deformation. System with lowest viscosity has less resistance to flow and require a reduced amount of applied force to get deformed (Fig. 5.6 (b)). Hence CTAB necessitate larger stress than other surfactants and DDAB requires less stress to get deformed.

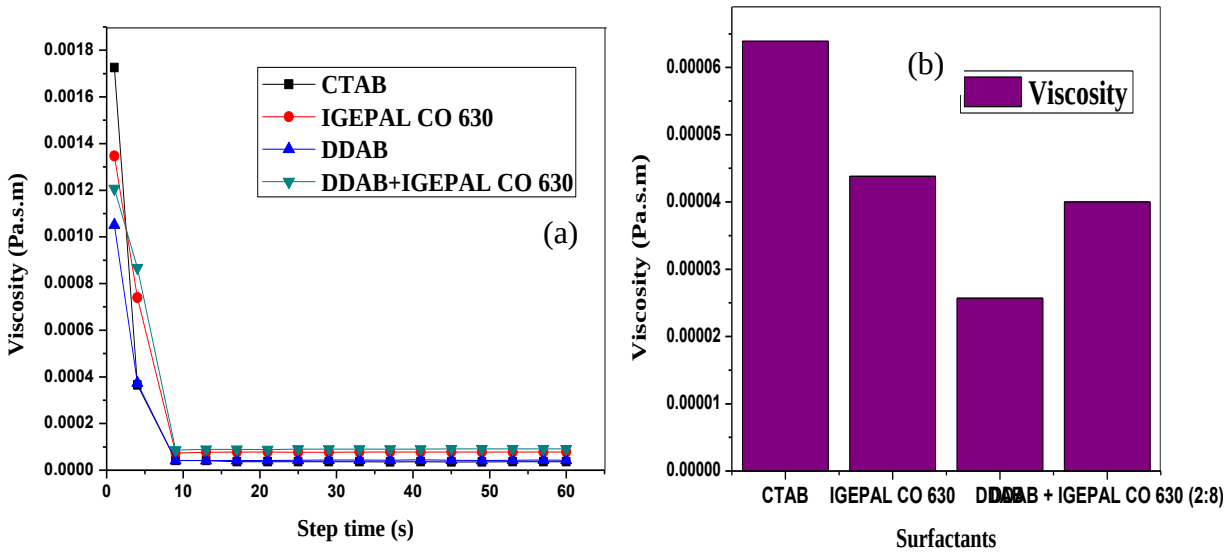


Fig. 5.7: Variation of viscosity with (a) time and (b) different types of surfactant and their mixture.

The surfactant solutions at air/water interface explain non-newtonian shear thinning thixotropy behavior which can be depicted from Fig. 5.7 (a) as viscosity is reducing with time. Viscosity is reducing after the perturbation of the micellar system and attains a fixed reduced value and remains constant at that particular point. Consequently the surfactant solution has a time dependent rheological behavior at the air-liquid interface which is advantageous in many industrial applications.

Table 5.2 surface tension, CMC & viscosity values of different surfactant systems.

Surfactants	**CMC (mM)**	**Surface tension(mN/m)**	**Viscosity (Pa.s.m)**
CTAB	0.98	37	6.39E-05
IGEPAL CO 630	0.041	32.5	4.38E-05
DDAB	0.039	28.195	2.57E-05
DDAB + IGEPAL CO 630 (2:8)	0.035	30.521	4.00E-05

Storage (G') & loss (G") modulus variation with angular frequency

Modulus can be directly linked with vicoelastic property of a fluid. Fig. 5.8 has been taken up to demonstrate storage (G') and loss (G") modulus variation with angular frequency at constant amplitude. The results can be inferred as, with decreasing surface tension of surfactants causes subsequent reduction in modulus. Storage and loss modulus describes stress response of a viscoelastic fluid in oscillatory shear. G' portray the elastic behavior of the fluid whereas G" explains the viscous response of the system. For every surfactant system loss modulus has lower magnitude than storage modulus signifying the elastic behavior of the system due to the presence of surfactant film at the air/water interface.

For a viscoelastic fluid system stress & strain can be represented as the following terminology

$$\text{Strain } (\gamma) = \gamma_o \sin(\omega t) \qquad (5.5)$$

$$\text{Stress } (\tau) = \tau_o \sin(\omega t + \delta) \qquad (5.6)$$

Where $\omega = 2\pi f$, where f is frequency of strain oscillation,

t = time,

δ = phase lag between stress and strain.

In the oscillatory regime the relationship between stress, strain and shear complex modulus is given by equation (8) [20].

$$\frac{\tau}{\gamma} = G' \sin(\omega t) + G'' \cos(\omega t) \qquad (5.7)$$

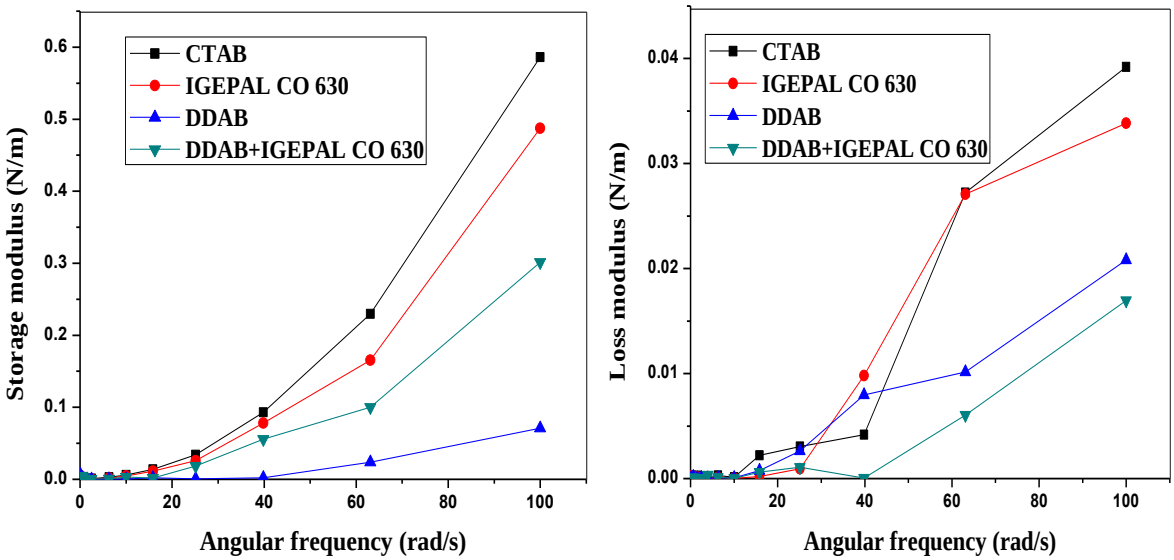


Fig. 5.8: Variation of (a) storage (G') modulus (b) loss modulus (G") with angular frequency at air/liquid interface in presence of different surfactant and their mixture.

Equation (5.7) implies the direct variation of modulus with viscosity. Decrease in modulus at air-water interface signifies decrease in viscosity contributing to the stability of the system.

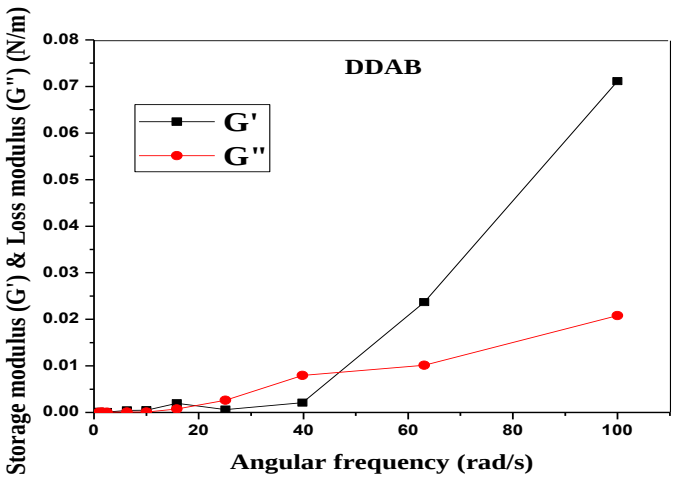


Fig. 5.9: G' & G" variation with angular frequency at air/liquid interface in presence of DDAB.

Above all for every surfactant system the elastic behavior is dominant except for DDAB as shown in Fig.5.8. After attaining the critical frequency the storage & loss modulus do cross each other indicating both viscous and elastic nature of the system. This attributes to the fact that lower the surface tension contributes to viscoelastic nature of micellar solution. From these studies it is clear that interfacial rheology is far more different than bulk rheology. One noticeable difference in simple language we can say that with the addition of surfactant the viscosity of bulk solution will increase but at the interface the viscosity will decrease.

6 EFFECT OF ELECTROLYTE ON RHEOLOGY OF CATIONIC SURFACTANT AT AIR/WATER INTERFACE

This chapter elaborates the effect of added electrolyte on the surface tension of cationic surfactant CTAB and on the flow behavior of surfactant solution at the air/water interface studied by rheology experiment. Focus has been given on the basic mechanism of the enhancement obtained due to the addition of electrolyte to the surfactant solution.

6.1 Introduction

The importance of electrolyte has already been discussed in previous chapters. The major aim of this study is to reduce the surface tension by adding electrolyte to the surfactant solution. To interpret how surface tension reduction is helping viscosity drop of the system. Different rheological parameters have been studied at the air/water interface to elucidate the flow behavior of the solution. Cationic surfactant has been chosen as it is ideal to use with electrolytes because only counter ions helps in reduction of electrical double layer. For anionic surfactant addition of electrolyte results in precipitation and increasing co-ion has no effect on rheology and surface tension reduction. Non-ionic surfactant doesn't possess any kind of charge showing no interaction with electrolyte. In the previous chapters we have used two cationic surfactant, one is double chain DDAB and single chain CTAB. DDAB has lowest CMC and surface tension value at CMC is also lower still we have chosen CTAB to carry forward the study as DDAB is much costlier than CTAB and its environmental impact is also high. So by any means if we are able to reduce the CTAB consumption to accomplish the desired goal will be more economical and environment friendly. NaCl is used as electrolyte salt as it is cheaper and also sodium salts are environment friendly.

6.2 Materials

The properties of CTAB and NaCl used are same as described in chapter 4.

6.3 Methods

The surface tension studies are same as described in chapter 4 and all rheological measurements are same as explained in chapter 5.

6.4 Results and discussion

6.4.1 Surface tension study of CTAB & NaCl solutions

The surface tension study has already been explained in chapter 4 and the surface tension values of CTAB with NaCl (10mM, 50mM, 200mM) are depicted from the solubilization graphs obtained from Fig. 4.4 (a) and are tabulated in Table 4.1.Addition of electrolyte even in small concentration to the surfactant solution makes it more thermodynamically stable and reduced surface tension at air/water interface is observed as the energy required to increase the surface area is decreased. The depression of CMC with increasing electrolyte may be due to reduced thickness of ionic atmosphere around the cationic head group and consequent decreased repulsion between the head group.

6.4.2 Rheology studies of CTAB & NaCl adsorbed at air/water interface

The transient behavior after onset of flow illustratesthe interfacial rheological parameters of surfactant solution. To initiate the flow a step function shear rate is applied at time zero and all parameters are obtained as a function of time.

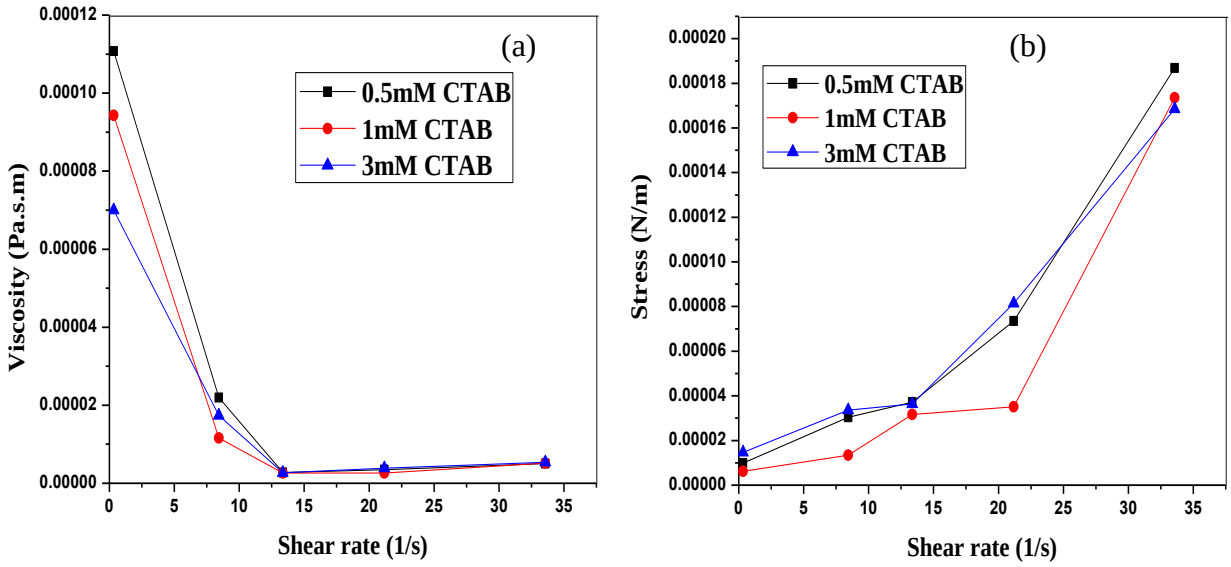


Fig. 6.1: Variation of (a) viscosity and (b) stress with strain at air/liquid interface in presence of CTAB.

The results are consistent with the studies done on previous chapter showing decrease in viscosity and stress values with strain as well as with increasing surfactant concentration. Fig. 6.1 signifies with increasing surfactant concentration the viscosity of the system is decreasing so as the stress values, proceeding towards a more stable system. We can see that as the system gets more stable the shear thinning thixotropy behavior is decreasing.

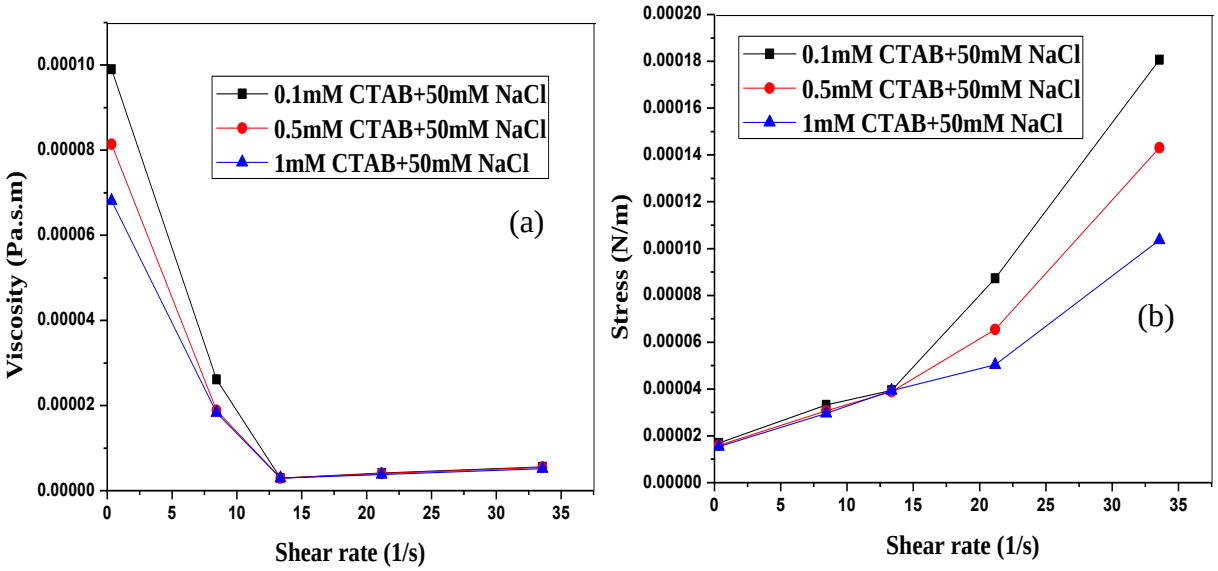


Fig. 6.2: Variation of (a) viscosity and (b) stress with strain at air/liquid interface in presence of CTAB & NaCl.

Addition of electrolyte (Fig. 6.2) shows synergism with CTAB solution and it can be noticed as presented in Table 6.1 that viscosity has lower value with NaCl added system than pure CTAB system.

Table 6.1viscosity values of CTAB and CTAB+NaCl system.

CTAB Concentration (mM)	Viscosity (Pa.s.m)
0.5	1.11E-04
1	9.43E-05
3	7.00E-05
0.1mM CTAB+50mM NaCl	9.90E-05
0.5mM CTAB+50mM NaCl	8.14E-05
1mM CTAB+50mM NaCl	6.81E-05

As viscosity is directly linked with energy of the system addition of electrolyte reduces the energy of the system making it stable and reducing the viscosity. Table 4.2 can be considered to obtain some fact that the viscosity that we have achieved at 1mM of CTAB that value can nearly be achieved at 0.1mM of CTAB with addition of 50mM NaCl. This can be attributed to the piece of information that use of electrolyte greatly reduces the surfactant concentration for a given duty.

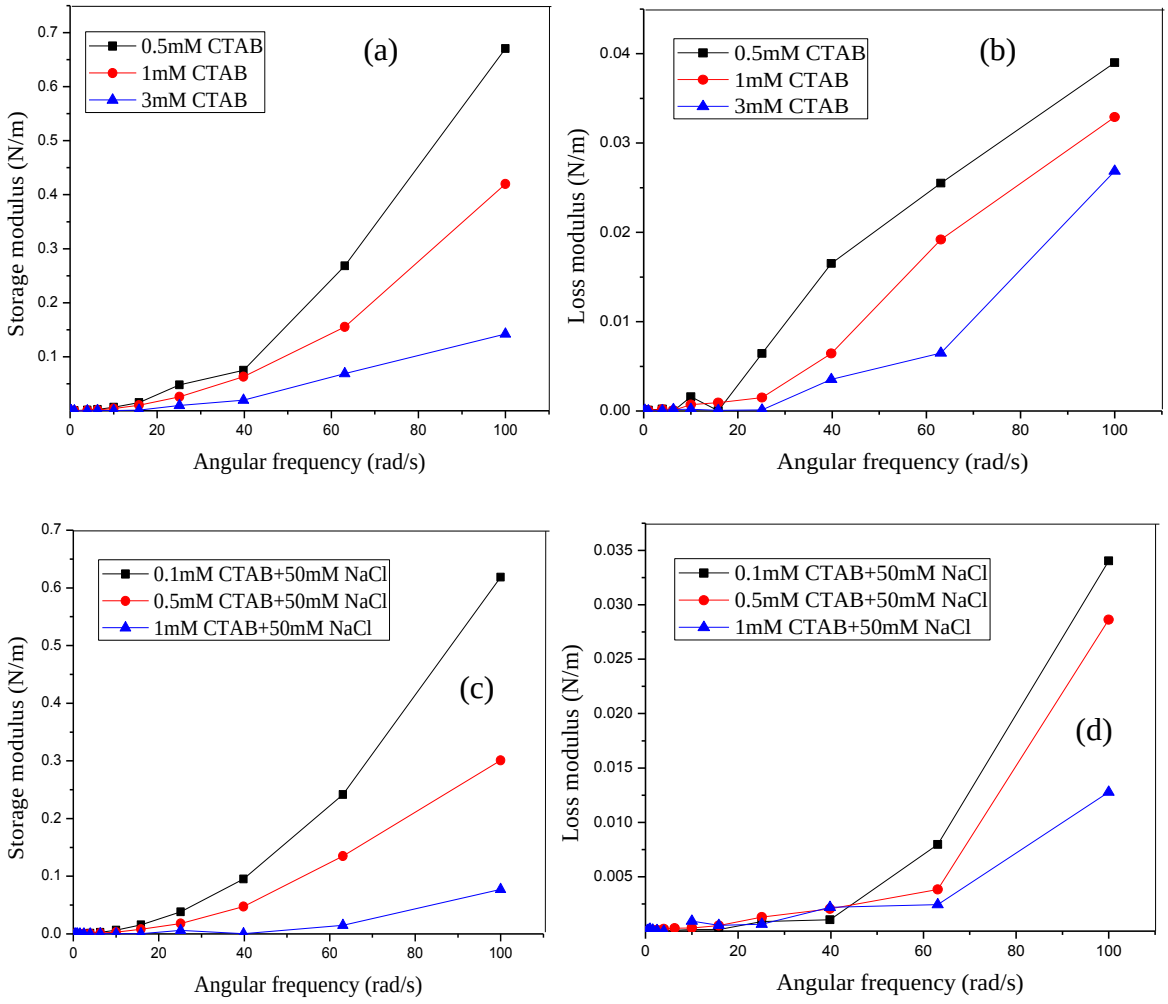


Fig. 6.3: Variation of storage modulus for (a) pure CTAB & (c) CTAB with NaCl and loss modulus for (b) pure CTAB & (d) CTAB with NaCl with varying angular frequency.

Fig. 6.3 gives the modulus values with varying angular frequency and constant amplitude. The modulus data depicts that CTAB surfactant solution exhibit elastic behavior as all the storage

modulus magnitudes are greater than loss modulus. The CTAB monomers at the air/water interface forms an elastic film. But with addition of electrolyte the curves move towards the region of viscoelasticity. Addition of electrolyte causes reduction of charge density around the micelles so as to reduce the energy at the interface causing stability of the system. Reduced modulus values with increasing CTAB concentration and CTAB with electrolyte justifies the above statement.

7 RHEOLOGY AT OIL/WATER INTERFACE IN PRESENCE OF ANIONIC SURFACTANT AND NANOPARTICLE

This chapter focused the effect of TiO_2 nanoparticle on the stabilization of oil/water interface in presence of anionic surfactant SDBS. Surface tension studies as well as shear and oscillatory rheology experiments has been carried out in this chapter in order to get a clear idea about the flow behavior of nanofluid and its stabilization by surfactant in presence of oil which is of great concern for many industrial application.

7.1 Introduction

The high surface activity of nanoparticles is the most important property to use it in many applications. For this particular study TiO_2 nanoparticle has been chosen. TiO_2 mineral can be found from nature easily. It has a wide range of applications in paint, food, drugs, and cosmetics. TiO_2 is one of the key ingredients in sunscreen which protects skin from sun's harmful UV-radiation. It is used as a colouring agent in food and other industries due to its white colour, in addition to that it can be used as flavor enhancer. Applications where opaqueness and transparency are major factors to concern, $TiO_2$is being used as it can absorb, reflect or scatter the light. In commercially manufactured products TiO_2 is considered as a safe ingredient as it does not penetrate through healthy skin. Another advantage of $TiO_2$is chemical inertness.

The key purpose of this study is to study the effect of nanoparticles on rheology at oil/water interface along with the presence of anionic surfactant sodiumdodecylbenzene sulfonate. $TiO_2$is used as nanoparticles as it has wide applications in cosmetics, pharmaceuticals industries and also used as a coating agent because of its transparent appearance. As TiO_2surface is positively charged it is expected that it will show synergism with anionic surfactant. SDBS has comparative lower CMC than other conventional anionic surfactants, hence considered suitable for this study.

7.2 Materials

Anionic surfactant sodiumdodecyl benzene sulfonate (SDBS, purity > 99%) and TiO_2 of 21nm (purity > 99.5%) were purchased from Sigma Aldrich. All the solution were prepared using ultrapure water (Sartorius, Germany) of 18.2MΩ·cm resistivity, 71.5 mN/m surface tension, and 6.5-7 Ph at 25 ± 0.5 °C.

7.2.1 Properties of surfactant used

SDBS

Sodium dodecylbenzenesulfonate is an anionic surfactant with molecular weight 348.48g/mol and has a molecular formula $CH_3(CH_2)_{11}C_6H_4SO_3Na$. It is a water soluble surfactant. It has amolecular structure as shown in Fig. 7.1. The theoretical CMC of IGEPAL CO 630 is around 1.6-2.7mM.

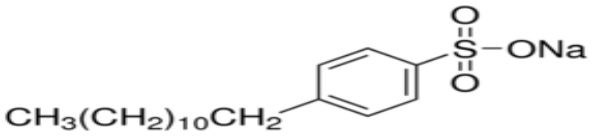


Fig. 7.1: Molecular structure of SDBS.

TiO_2nanoparticle

Also known as titanium (IV) oxide or titania. TiO_2 nanoparticle used is of 21nm and has a molecular weight of 79.87 g/mol.

7.3 Methods

All the surface tension and rheology experiments are same as described in chapter 5.

7.4 Results and discussion

7.4.1 Surface tension studies of SDBS and TiO_2 solutions

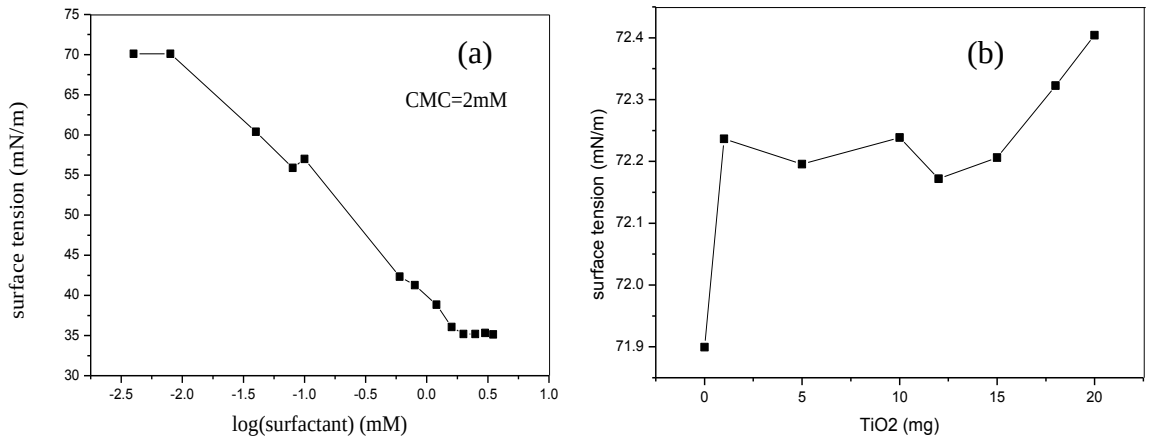


Fig. 7.2: surface tension vs. (a) SDBS (b) TiO_2 concentration.

It can be seen from Fig. 7.2 (a) that the high surface tension of water is decreasing from 72mN/m to 35mN/m with the addition of anionic surfactant SDBS of 2-3.5mM and its CMC was found to be 2mM. TiO_2 (21nm) concentration has not much effect on surface tension of water (Fig. 7.2 (b)). On the other hand the surface tension of water increases with increasing concentration of TiO_2. The possible explanation may be nanoparticle with low concentration has little effect on surface tension because the distance between the nanoparticles is quite large even at air/liquid interface. Elevated particle concentration results in increasing van der waals force between the particles at air/water interface. Consequently surface free energy increases and hence increase in surface tension ensued [54].

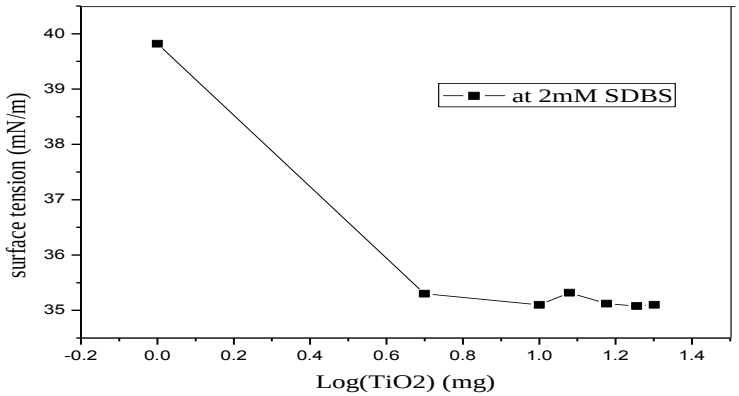


Fig. 7.3: effect of SDBS (2mM) on surface tension values of TiO_2.

DLS experiment confirmed that the TiO_2 nanoparticle used in this study has positively charged surface as the zeta-potential comes to be 5.88. High surface energy due to nano sized particles leads to instability at the interface, therefore surfactants are used to decreases the surface energy required to increase the surface area. After addition of surfactants it can be observed from Fig. 7.3 that surface tension decreases with the addition of SDBS as compared to the base fluid. Decrease in surface tension is may be due to electrostatic repulsive force among the particles, due to the presence of surfactant monomer layer adsorb to nanoparticle resulting decrease in surface energy and hence surface tension [54].

7.4.2 Oscillatory & shear rheology studies at oil/water interface

Rheology studies of SDBS solution

Fig. 7.4 shows that all the nature of the curve agrees well with the rheology results obtained in the preceding chapters. The major change in all cases occurs at low strain region. Fig. 7.4 (b) can directly correlate viscosity with strain.We can say that with applied strain rate viscosity is reducing.

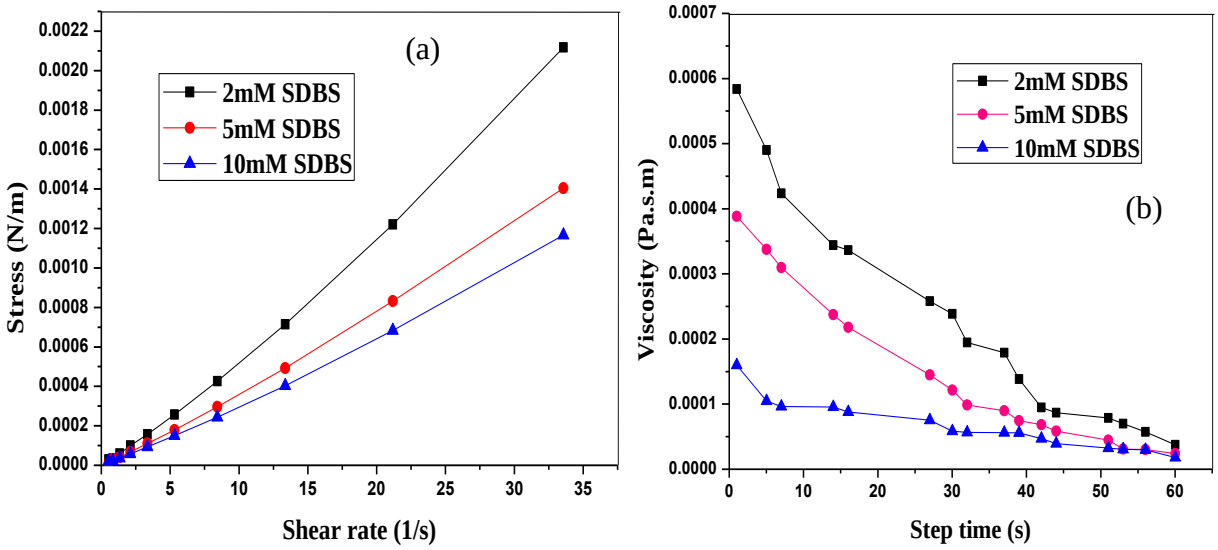


Fig. 7.4: variation of (a) stress and (b) viscosity with shear rate and time for SDBS solution.

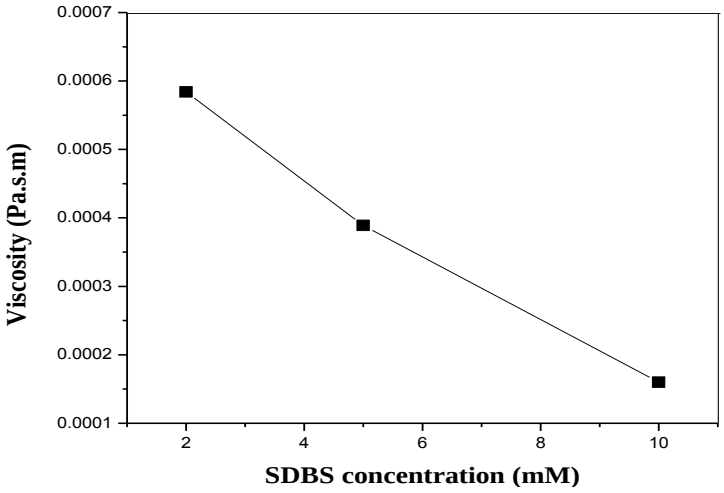


Fig. 7.5: variation of viscosity with increasing concentration of SDBS.

With increase in SDBS concentration viscosity gradually decreases as can be seen from Fig.7.5. With increase in surfactant concentration results in reduction of interfacial tension lowering the energy of at the interface so time with applied strain on increasing the surfactant concentration viscosity is reducing. Viscoelasticity is the characteristic nature of the surfactant solution and this

result also justifies this fact. At low surfactant concentration viscosity is high may be due to the fact that the interfacial area is quite small compared with surfactant with high concentration, hence surfactant spread more thinly. Interfaces with small surface area have higher energy and they give rise to higher viscosity.

Rheology studies of TiO_2 solution

The results represented in Fig. 7.6 are quite contradictory obtained from surfactants. The viscosity is increasing with increasing TiO_2concentration (Fig. 7.6 (b)) although the viscosity values are much lower than the SDBS viscosity values as represented in Table 7.1. The decreasing trend of viscosity with increasing strain reflects shear thinning thixotropy behavior of the nanoparticles suspension at the oil/water interface.

As a nanoparticle has many more molecules on its surface than bulk compared to larger particles, nanoparticles possess higher surface energy. Particle with high surface energy when brought into contact with another liquid or particle adhesive and cohesive force of interparticle attraction is high. Hence with increasing concentration of TiO_2 viscosity is increasing as it is directly related to energy of the system. Considering only the particles, at high surface energy the van der wells force of attraction increases between the particles and henceforth increasing concentration of TiO_2 (21nm) nanoparticles approaches towards agglomeration. Hence to break such agglomeration surfactants are used to show synergism. Despite of the increase in viscosity the nanosuspension is requiring nearly same amount of stress (applied force) to get deformed.

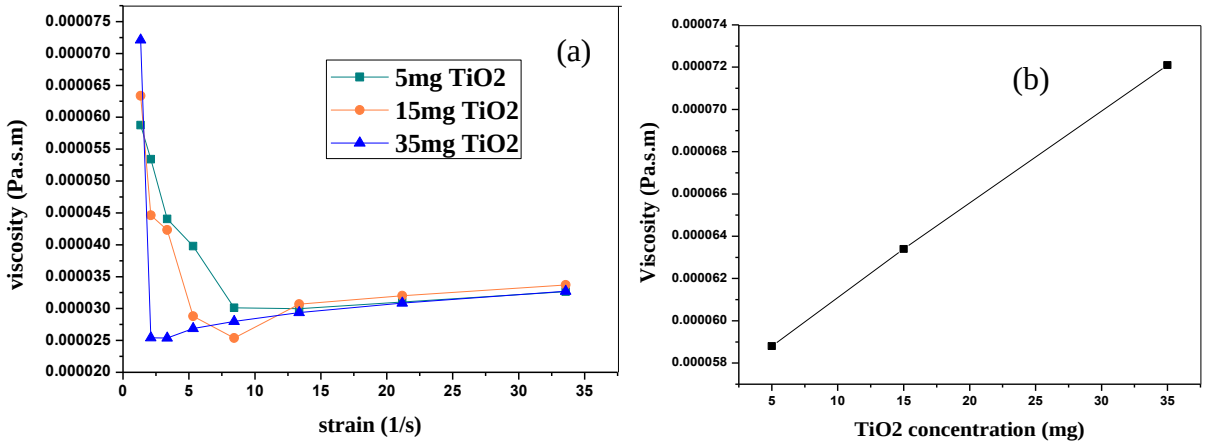


Fig. 7.6: Viscosity variation of TiO_2solution at oil/water interface with (a) strain (b) TiO_2concentration

Table 7.1 The viscosity values for different SDBS and TiO_2 system

Concentration	Viscosity (Pa.s.m)
2mM SDBS	5.84E-04
5mM SDBS	3.89E-04
10mM SDBS	1.60E-04
5mg TiO_2	5.88E-05
15mg TiO_2	6.34E-05
35mg TiO_2	7.21E-05
10mM SDBS+5mg TiO_2	2.01E-04
10mM SDBS+15mg TiO_2	1.47E-04
10mM SDBS+24mg TiO_2	7.49E-05
20mg TiO_2 +5mM SDBS	1.28E-04
20mg TiO_2 +10mM SDBS	1.06E-04
20mg TiO_2 +15mM SDBS	6.56E-05

Smaller the particle size larger the surface potential required to have a stable dispersed medium. To accomplish this goal surfactants are used as they possess unique structure and controlled adsorption at the particle surface.

Rheology studies of varied $TiO_2$and constant SDBS systems

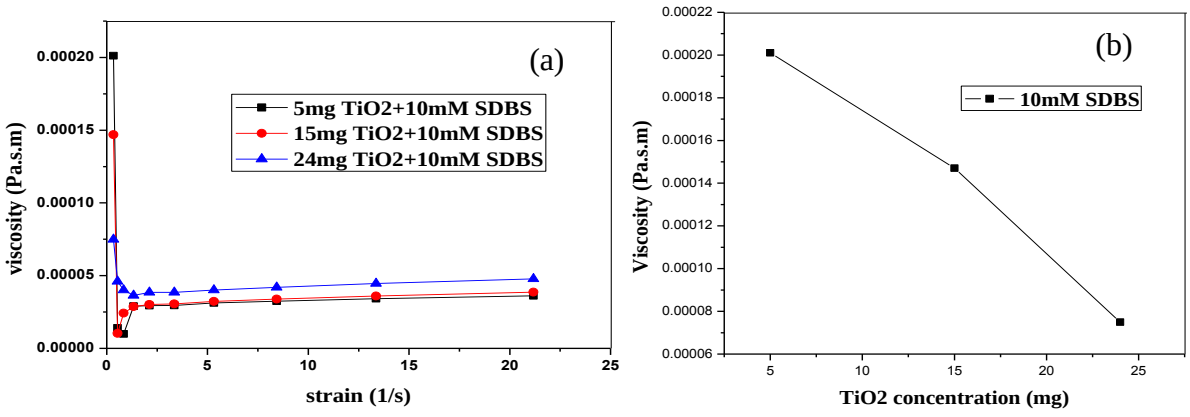


Fig. 7.7: Viscosity variation of TiO_2solution at oil/water interface in presence of 10mM SDBS with (a) strain (b) TiO_2concentration

With increasing TiO_2nanoparticle the viscosity is reducing at constant SDBS (10mM) concentration at the interface as inferred from Fig. 7.7. With increasing strain the viscosity drops suddenly and attains a plateau level with no further reduction of viscosity occurred. With increasing strain stress is increasing and with increasing TiO_2 stress is reducing. As the viscosity plot is against strain rate with respect to step time it can be inferred that the solution is showing non-newtonian shear thinning thixotropy behavior as viscosity is reducing with step time. From all the results obtained it is worth mentioning that at low shear rate viscosity is decreasing and at high shear rate all the viscosity data move towards a single final value.

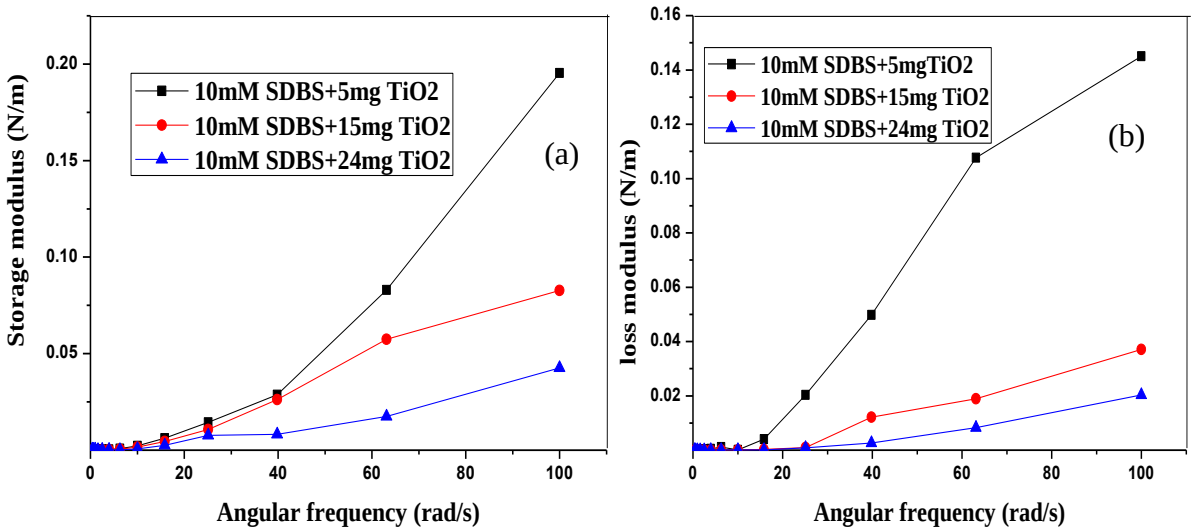


Fig. 7.8: Variation of (a) storage (G') modulus & (b) loss (G") modulus with angular frequency for TiO_2adsorbed at oil/water interface in presence of 10mM SDBS.

For varied TiO_2system with increasing concentration both storage and loss modulus are decreasing (Fig. 7.8). But in every case the storage modulus is greater than the loss modulus showing elastic behavior of the solution containing both nanoparticles and surfactant and may be the elastic behavior is due to the adsorbed surfactant monomer at the nanoparticles surface. There should be sufficient monomer present to adsorb at the nanoparticles surface so that particle agglomeration can be inhibited due to the presence of electrostatic repulsion between the head groups. This helps in well dispersion of the stable oil/water system. Therefore increasing the surfactant concentration at constant TiO_2 is preferred to get the desired result.

Rheology studies of constant $TiO_2$and varied SDBS systems

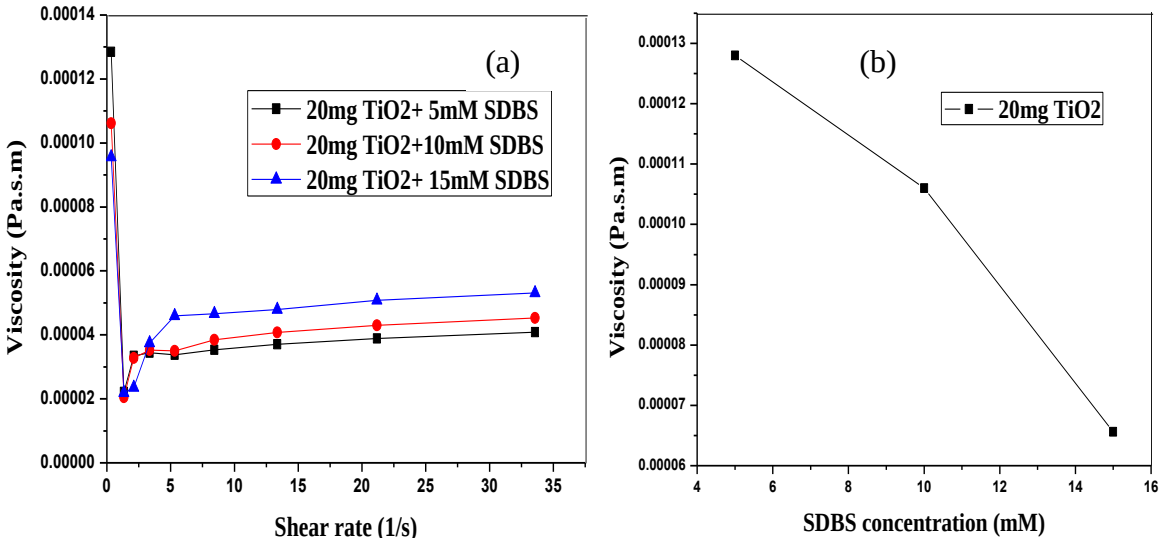


Fig. 7.9: Viscosity variation of SDBSsolution at oil/water interface in presence of 20mg TiO_2 with (a) strain (b) SDBSconcentration

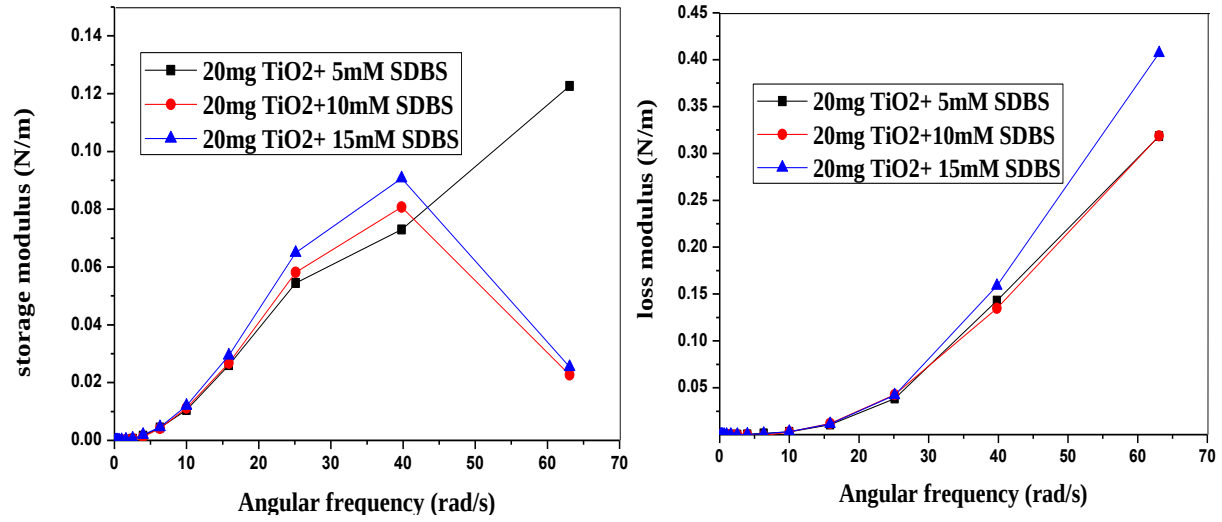


Fig. 7.10: Variation of (a) storage (G') modulus & (b) loss (G") modulus with angular frequency for SDBSadsorbed at oil/water interface in presence of 20mg TiO_2.

Same results obtained (Fig.7.9)as previous but increasing the SDBS concentration keeping TiO_2 constant has shown more synergistic performance than the former one as viscosity values are smaller than the constant SDBS system as tabulated in Table 7.1. For varied surfactant system (Fig.7.10) at higher surfactant concentration the storage modulus falls down suddenly from a

maximum value, whereas the loss modulus is keep on increasing with increased angular frequency. In every case the loss modulus is higher than the storage modulus implying viscoelastic property.

For 20mg TiO_2 and 15mM SDBS system G' has higher value than G" but after some critical frequency G" curve crosses G' curve depicting viscoelasticity nature of the nanopartticle/surfactant stabilized oil/water interface.

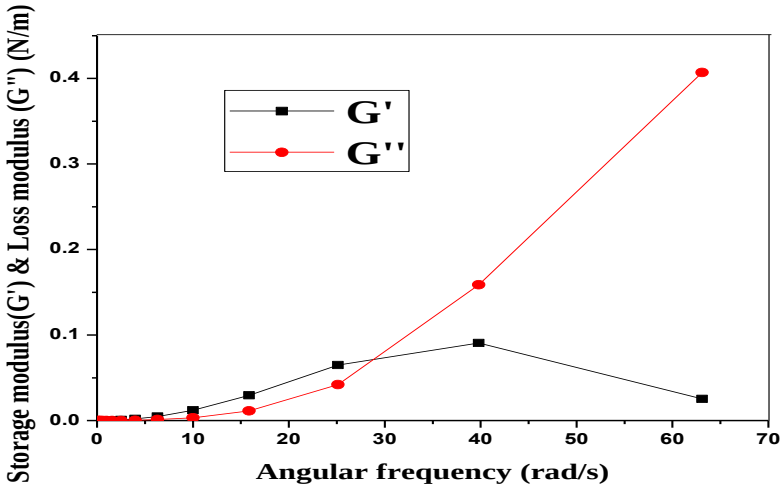


Fig. 7.11:storage & loss modulus behavior of 20mg TiO_2+ 15mM SDBS

Increasing the surfactant concentration contributes to quick increase in oil/water interface stability especially at 10-15mM SDBS concentration (Fig 7.11). At low surfactant concentration the repulsive force between nanoparticles is very less but with increasing surfactant concentration steric repulsive force arise contributing decrease in viscosity and linear viscoelastic parameters. Decrease in modulus with increasing surfactant concentration attributes to the fact that repulsive force increase overcoming the van der waals force causing reduced viscosity at the system and more stable oil/water interface.

8 CONCLUSION AND FUTURE SCOPE

In this chapter, major conclusions drawn from the research work carried out in the thesis has been presented. Scope for future research on additive based enhanced solubilization and rheological behavior for optimum stability has also been suggested.

8.1 Conclusion

The following conclusions can be drawn from the following study:

- Anthracene has much lower solubilization than naphthalene because of its high molecular weight as it contains three benzene rings. PAHs with higher number of aromatic rings has lower solubilization in a given surfactant concentration.
- Cationic surfactant is best suited with electrolytes. Using electrolytes with surfactants one can achieve the reduced surface tension at a much lower surfactant concentration. The mechanism of using higher valence electrolytes with cationic surfactant to reduce the consumption of toxic and costly surfactant can be widely accepted from both economic and environmental point of view.
- Among all the electrolytes used Na_2SO_4 is gives higher solubilization at far more less concentration of surfactant.
- Among DDAB, CTAB, IGEPAL CO 630, DDAB has the lowest CMC with low surface tension hence more effective in reducing the viscosity at air/water interface making the system stable.
- To reduce the environmental impact and to have an economical aspect IGEPAL CO 630 mixed with DDAB has shown synergistic effect as observed by rheological parameters.
- The viscosity and complex modulus values can greatly be reduced with the application of electrolyte with cationic surfactant CTAB.
- Nanoparticles can give more stable system than surfactant system as the viscosity values are much less than the viscosity value obtained with SDBS adsorbed at oil/water interface.
- As the nanoparticles are highly unstable, to get a stable system addition of surfactant is the most efficient way to have a system with thermodynamic stability.

- The Positively charged TiO_2mixed with anionic surfactant SDBS has shown synergism.

8.2 Future scope

- To have optimum solubilization other additives such as polymer, co-surfctants can be added to the system. Solubilization of other hydrophobic substance such as oil can also be considered depending on other applications.
- DDAB and IGEPAL CO 630 ratios can be varied and the best possible ratio can be determined in order to reduce both surface tension and CMC
- Their rheological studies can be performed at oil/water interface with different additives
- Other nanoparticles can be used to study the synergism with different surfactant depending on the surface charge of nanoparticles and charge of the surfactant head group.

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